KINETICS AND MECHANISM OF OSMIUM TETROXIDE CATALYSED OXIDATION OF SOME CYCLIC ALCOHOLS BY CHLORAMINE-T

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CERTIFICATE

This is to certify that the thesis entitled, "KINETICS AND MECHANISM OF OSMIUM TETROXIDE CATALYSED OXIDATION OF SOME CYCLIC ALCOHOLS BY CHLORAMINE -T", submitted for the degree of Doctor of Philosphy of Bundelkhand University Jhansi U.P is a record of bonafide research work carried out by Manoj Dwivedi under my guidence and supervision. He has worked under me for the required period under research ordinence7 of Bundelkhand University Jhansi. He has put in the required attendence in his department during that period.

The work embodied in this thesis or a part there of, has not been submitted for the award of any other degree or diploma. All the help and assistance received during the cource of present investigations have been duly acknowledged.

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Manoj Dwivedi

(Manoj Dwivedi)

CONTENTS

CHAPTER-1

INTRODUCTION

1.1 : GENERAL

Any attempt to understand the mechanism of a chemical process requires knowledge of elementary processes involving atoms, molecules and ions that participate simultaneously or consecutively in producing the observed overall reaction[1]. Kinetics, a branch of physical chemistry, is an important and effective tool to deal with the role of all factors which may influence the velocity of a chemical reaction under investigation. The observed effect in the rate of the reaction is explained in terms of reaction steps, called reaction mechanism.

Chemical reactions of wider application have attracted the attention of several scientists since long period for showing their interest in evolving or suggesting the mechanism of such reactions. The scientists engaged in such endeavour have employed the kinetic observations gathered in their studies to achieve their aims to large extent. Their interest in such studies is based on the vast applications of such reactions in several fields such as industries, agricultural problems and medicinal zones. For a chemist the importance of a kinetic study lies in the fact that by understanding the dependence of the various reactions on different reaction variables such as concentrations of various species involved in the chemical process, temperature, solvent dielectric constants, ionic strength of the medium, solvent isotope etc., one can

control the course of formation of products of a chemical reaction with such parameters. Thus a researcher in this field can find out the conditions required for favouring a desired product. A knowledge of the mechanism by which the reactants are converted in to products is of great value and the study of kinetics of the reaction coupled with other techniques offers one of the most satisfactory and successful ways for obtaining information about the path ways involved in a particular reaction. The present interest of chemists in kinetics is due to precise and careful interpretation of kinetic data collected under different conditions. The numerous scientific publications of difficult and complicated reactions have helped in acquiring further developing confidence in researchers. The scientists with such an amount of confidence have been able to solve many difficult reactions mechanism.

The most thoroughly probed reactions in solutions from kinetic points of view have been redox systems. It is customary to represent generally the redox reactions as electron transfer reactions in inorganic chemistry while transfer of atoms or ions is involved in most of the organic redox systems. The presence of a considerable solvation barrier formed by the surrounding water molecules around the ions has ruled out the direct electron jump from the reactant to oxidant molecules in solution, while during oxidation-reduction process the transfer of atoms or ions between the species involved is supported by experimental

facts. The mechanism based on such transfer of atoms or ions seems to be quite reasonable.

The studies of radioactive exchange between two species in different oxidation states involving no net chemical reactions also support the mechanism of transfer atoms or ions.

Thus oxidation process is accompanied by transfer of hydrogen species such as hydrogen atom or hydride ion but not the proton, while the transfer of oxygen species such as oxygen atom but not oxide or hydroxide ion and transfer of chlorine species such as chlorine atom or chlorinium ion but not chloride ion brings about reduction. Although in many inorganic redox systems electron transfer alone has been reported to cause a change in the oxidation state of donor and recipient, but recent reports indicate that electron transfer is by no waves the only favored route used by such powerful oxidants as permanganate ion and chromic acid. Thus kinetics provides a very interesting tool to identify the routes or paths of reactions and is time dependent[2].

In order to elucidate the satisfactory mechanism of reactions in solution, considerable informations are required. These informations can be collected by studying the effect of several factors that may or may not influence the rate of the reactions. If kinetics is taken as basic tool for the study of mechanism of such reactions, then one important factor is the order of the reactions with respect

to all possible species involved in the chemical reactions. The studies of effect of ionic strength of the medium[3] effect of solvent[4] and effect of variation of dielectric constant[5] of the medium and temperature variation effect on the rate of the reactions are also important information which guide in evolving a suitable and convincing mechanism of the reactions. The structures and identifications of intermediates and other informations about them and use of isotopic method[6] immensely help in establishing the real reactions routes followed in a chemical reaction. Finally, on the basis of such above mentioned informations, the rate law is derived with the help of suitable possible assumptions and thus better and clear insight of the mechanism of the chemical reaction is exposed.

Bomford and Trapper[7] have discussed a detailed account of a large number of familiar and less familiar redox reagents in a recent publications. In another publications, Berke and Zyka[8] have also discussed several less familiar and newer redox titrants. The authenticity of the proposed mechanism on the basis of aforesaid informations is, further, strengthened by isolation, characterisation and identification of the final reaction products it is thus possible to visualise many intermediate products which are although very reactive but at the same time short lived. The existence of such valuable short lived intermediates or free radicals can be demonstrated by the addition of radical traps or scavengers[9] such as allyl acetate, vinyl

monomers which readily combine with the free radicals. These free radicals can also be identified by informations obtained from electron paramagnetic resonance (EPR)[10,11] studies.

The oxidising and reducing capacity of a compound is often determined by its redox potential from which the knowledge of free energy available for a redox reaction can be obtained. However, this knowledge is not ultimate as there are several other factors which affect the rate of a reaction. In recent studies it is reported that an increase in electronegativity causes reduction while an increase in electropositivity brings about oxidation. Thus oxidation and reduction processes are complimentary to each other and these processes take place simultaneously.

Recently, systematic reports[12-43] on kinetics and mechanism of several redox processes involving newer redox titrants have been made. The detailed investigations on a number of reactions catalysed by silver (I), copper (II), Osmium (VIII) and colloidal silver have been reported[22]. A recent study has been reported on the kinetics of oxidation of some α-hydroxy acids by chloramine-T using osmium tetroxide as catalyst.[25] Several aliphatic aldehydes and reducing sugars have been used as substrates for chloramine-T oxidation kinetics in alkaline media. Agrawal and Mushran have also discussed the oxidation of Hexacyanoferrate (II) by chloramine-T in acidic media. Recently Mehrota and Mushran have investigated the

mechanistic steps in the oxidation of monohydric primary and secondary alcohols by chloramine-T in acidic media with and without the use of osmium tetroxide as catalyst.

1.2: CHLORAMINE-T AS OXIDANT

Chloramine-T is known as sodium salt of N-chloro-p-toluenesulphonamide. It is less familiar but a very potent oxidising[42-44] agent both in alkaline and acidic media. A close survey of literature reveals that chloramine-T has been employed for the determination of numerous inorganic and organic substances. Although much work has been quoted in literature on this compound used as oxidant but still there is much scope to study the kinetics and mechanism of oxidation of various reducing substances using different kinds of catalyst with this oxidant both in alkaline and acidic media. Keeping this aim in mind, the present work envisages the investigation on the kinetics and mechanism of oxidation of a few cycloalcohols with chloramine-T using osmium tetroxide as catalyst in alkaline media and further, an attempt has been made to establish the mechanism and spell out the various intermediate steps involved in such reactions.

The aqueous solutions of chloramine-T if stored in dark, do not change their strength for several months[45] and hence are stable. It has been observed that solutions become cloudy due to slow decomposition with the formation of chlorinated sulphonic acids[46] in the presence of sunlight. This precipitate is not the same as the dichloramine-T thrown down in acid solution and pH falls to 5.6 from initial value of 7.7 over a year giving support to the

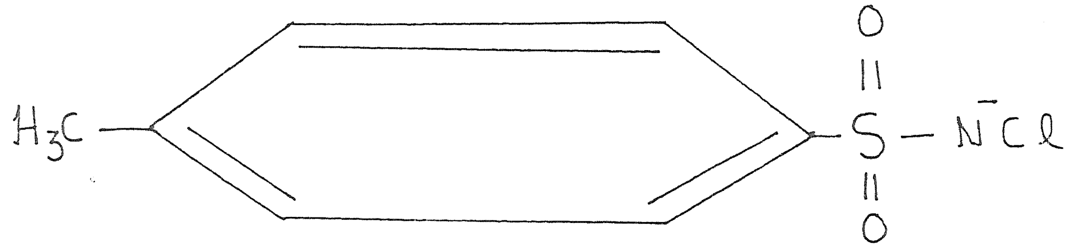
contention of dietzel and taufel that the photochemical self oxidation decomposition product of acidic in nature. According to Carlsen[47], the photochemical deterioration of chloramine-T solution is not detectable beyond 450 mμ. The hydrolysis of chloramine-T in water is often incompletely described so that chloramine-T and hypochlorite solutions are regarded as completely similar in properties. It follows that chloramine-T may be substituted directly for hypochlorite, or for bromate in the presence of bromide. iodate in the presence of iodine monochloride or iodine in the presence of iodide.

It has been reported[48] that chloramine-T hydrolysis in water according to the following equation.

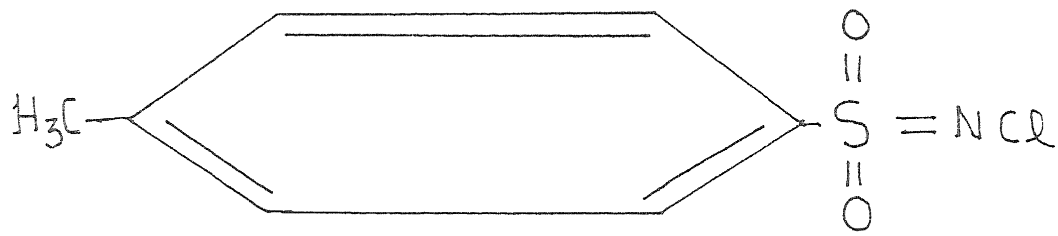
$$CH_3C_6H_4SO_2N\ NaCl + H_2O \rightleftharpoons CH_3C_6H_4SO_2NH_2 + Na^+ + ClO^- \quad ..(1)$$

The species in the right side of above equation (1) will ionise and except in alkaline medium, the hypochlorite ion will hydrolyse to hypochlorous acid which is assumed to be oxidising species as described above. Most of the publications on chloramine-T deal with qualitative properties and pharmaceutical[49] use of the reagent and its[50-51] stability. However recent publications on chloramine-T have discussed mostly the kinetic behaviour of the reactions. In the present investigation an attempt has been made to reveal the kinetic observations on which basis the reaction routes have been proposed.

The structure of chloramine-T is generally described as (A) and occasionally as (B)[52-53]



[A]



[B]

In addition to above, other reactions would take place as given below :

$CH_3C_6H_4SO_2N\ NaCl + H_2O \rightleftharpoons CH_3C_6H_4SO_2NHCl + NaOH$ ..(2)

$2CH_3C_6H_4SO_2N\ NHCl \rightleftharpoons CH_3C_6H_4SO_2NCl_2 + CH_3C_6H_4SO_2NH_2$ ..(3)

$CH_3C_6H_4SO_2NCl_2 + NaOH \rightleftharpoons CH_3C_6H_4SO_2NHCl + NaClO$ ..(4)

$CH_3C_6H_4SO_2N\cdot NHCl + NaOH \rightleftharpoons NaClO + CH_3C_6H_4SO_2NH_2$ ..(5)

hypochlorous acid is formed as a result of hydrolysis of sodium hypochlorite in an acidic or neutral media.

$NaClO + H_2O \rightleftharpoons NaOH + HClO$ ..(6)

Some of researches such as Bishop and Jennings[50] Soper[54], dietzel[48] et al and Morris et al[55] have reported that quite different equilibria exist in the hydrolysis of chloramine-T Accordingly, Chloramine-T has been described as strong electrolyte which first dissociates.

$CH_3C_6H_4SO_2N\cdot NaCl \rightleftharpoons CH_3C_6H_4SO_2NCl^- + Na^+$ ..(7)

the anion thus formed takes up hydrogen ion to form the free acid which disproportionates to give p-toluene sulphonamide and sparingly soluble dichloramine-T.

$CH_3C_6H_4SO_2N\cdot HCl^- + H^+ \rightleftharpoons CH_3C_6H_4SO_2NHCl$ ..(8)

$2CH_3C_6H_4SO_2NHCl \rightleftharpoons CH_3C_6H_4SO_22NCl_2 + CH_3C_6H_4SO_2NH_2$ ..(9)

The dichloramine-T and free acid hydrolysis as

$CH_3C_6H_4SO_2NCl_2 + H_2O \rightleftharpoons CH_3C_6H_4SO_2NHCl + HOCl$ ..(10)

$CH_3C_6H_4SO_2NHCl + H_2O \rightleftharpoons CH_3C_6H_4SO_2NH_2 + HOCl$ ..(11)

The hydrolysis constant for these two reactions (10) and (11) are 8×10^{-7} and 4.88×10^{-8}. It appears that hydrolysis is therefore slight. Finally the hypochlorous acid ionises ($Ka = 3.30 \times 10^{-8}$). the concentration of

various species present in 0.05 M chloramine-T solution over a range of pH value are given by Bishop and Jennings[50], thus the nature of the main oxidising species of chloramine-T depends upon the pH of solution[48].

The solutions of chloramine-T can be standardised easily by the addition of potassium iodide and starch and titrating the liberated iodide by standard sodium thiosulphate solutions. Chloramine-T has also been employed for the direct titration of sodium arsenite using potassium iodide and starch.

In the estimation of halides, chloramine-T has also been used as a substitute for chlorine water. The redox potential of chloramine-T & p-toluene sulphchloramide system was reported by Afanas'ev as 0.90 Volt in the neutral solution and 1.52 Volts in 1N-H_2SO_4. Murthy and Rao have reported that redox potential for this system varies from 1.139 to 0.499 Volts for the variation of pH from 0.65 to 1.20. Noll has used chloramine-T as substitute for iodine in analytical chemistry.

Mahadevappa and coworkers have estimated rongalibe[56] thioglycollic acid[57], cystein[58], they have also estimated unsaturated alcohols such as allelic alcohols[59,60], crotyl alcohol[61] and cynnamyl alcohol[62] by chloramine-T.

1.3: KINETICS AND MECHANISM OF CHLORAMINE-T OXIDATION

Much work thus appears to have been done on exploring the importance of chloraminometric oxidation of a large number of compounds but literature on step by step oxidation with this oxidant under a variety of conditions is scanty.

Coul and coworkers[63] for the first time studied the kinetics and mechanism of hydrogen peroxide by chloramine-T in presence of hydrochloric acid. Logistic[64] function was used far the determination of the reaction rates. The rate law showed a first order dependence to hydrogen peroxides and chloramine-T and an inverse first-order in p-toluenesulphonamide concentration. They suggested a mechanism involving formation of chlorine as a result of interaction between chloramine-T and hydrochloric acid.

Kucsman and Coworkers[65] studied the kinetics and mechanism of reaction of substituted methyl aryl sulphides and diaryl sulphides with chloramine-T and proposed the mechanism of sulphilimine synthesis. Further, Modena and Coworkers[66] obtained similar results for the oxidation of same thioanisoles. Kinetics and mechanism of oxidation of glycerol by chloramine-T has been made by Weker and Valic[67] in neutral and alkaline media. The rate of the reaction was found to be independent of glycerol concentration and the reaction was autocatalytic in nature.

Higuchi and Hussain[68] have studied the kinetics of

chlorination of p-cresol by chloramine-T.

The kinetics of chloramine-T oxidation of secondary alcohols has recently been studied[69]. Mushran and Coworkers have recently reported oxidation of-α amino acids[27,70]. They have also studied the kinetics of oxidation of EDTA[28] by chloramine-T Banerjee[71] has studied the oxidation kinetics of primary alcohols-chloramine-T redox system in acidic media. Recently Santappa and Coworkers[72] have investigated decarboxylation chlorination of cinnamic and crotomic acids by chloramine-T in acidic buffered media. Radhakrishnamurti and Sahu[73] have studied the kinetics and mechanism of halogenation of benzaldehyde by chloramine-T in acidic media of pH 4.5. Carboxylic acids are the products at PH 4.5 in aqueous media where as halogenated benzaldehydes are formed in aqueous acetic acid sodium acetate buffer medium.

1.4 : PRESENT WORK

In the present thesis, an attempt has been made to study the kinetics and mechanism of oxidation of cyclopentanol, cyclohexanol, and 2-methyl cyclohexanol by alkaline solution of chloramine-T in the presence of osmium tetroxide as homogeneous catalyst. The main aim of the present investigation is to explore the catalytic species of osmium tetroxide in alkaline medium in chloramine-T-cycloalcohols redox systems and to interpret its catalytic role in elucidation of reaction mechanism of the reactions undertaken here.

1.5 : A SUMMARY OF KINETIC RESULTS AND RATE LAW DERIVED ON THE BASIS OF PROPOSED MECHANISM

The following kinetic observations have been recorded in osmium tetroxide catalysed oxidation of a few cycloalcohols by alkaline solution of chloramine-T.

(i) Oxidation of cyclopentanol, cyclohexanol and 2-methyl cyclohexanol shows first order dependence on oxidant which is chloramine-T.

(ii) First order dependence of all reactions on each of cycloalcohols was observed.

(iii) First-order kinetics with respect to sodium hydroxide was exhibited.

(iv) All reactions showed first-order with respect to osmium tetroxide.

(v) Negligible effect of change in ionic strength of reaction mixture on rate of oxidation of all cycloalcohols was observed.

(vi) Zero effect of addition of P-toluenesulphonamide (a reduction product of chloramine-T) on rate of reactions was observed.

(vii) Marked effect of rise in temperature on reaction velocity was observed.

On the basis of kinetic data, a suitable mechanism of proposed, which yielded the following rate law in agreement with kinetic observations..

$$-d[CAT]/dT = k\ [CAT][OH^-][OsO4][S]$$

where S = Cycloalcohols

CAT = Chloramine-T &

$k = k_2 k_3 k_1 / k_{-2} [H_2O]$

REFERENCES

1. R. Stewart, "Oxidation mechanism application to organic chemistry", M.A. Bezamin, New Yark (1964).
2. S.W. Benson, `The foundation of chemical kinetics', Mc Graw Hill Book Co., New Yark (1960).
3. J.N. Bronsted, Z. Phys.,Chem., 102, 169 (1922).
4. A.S. Amis,"Solvent effect on reaction rates and mechanism", Acad Press, New Yark. (1966).
5. D.E. William, J.Amer. Chem. Soc., 88,5665 (1966).
6. L. Milander,"Isotopic effects on reaction rates and mechanism, acad,Press, New York (1966).
7. H.C. Bomford and C.H.F. tripper,"Comprehensive chemical kinetics" vol.7, Elsevier, Publishing Co. New York (1972).
8. A.. Berka and J. Zyka, `Newer Redox Titrants, Pergamon Press, 1st Edition, 52 (1965).
9. J.C. Bailer, `Chemistry of Coordination compounds, Pg.,4, Reinhold, New York (1956).
10. H.M. Connel, Adv. in Phy. Chem., 8 (1958).
11. J.E. Wertz, Adv. in Phys. Chem., 9 (1958).
12. M.C. Agarwal et al, J. Indian Chem., Soc., 42, 629 (1965).
13. R.K. Singhal et al, Z. Phys. Chem. 62, 112 (1968).
14. S.P. Mushran, J. Indian Chem. Soc., 45, 526 (1968).
15. U.S. Mehrotra et al, J. Phys. Chem. 73, 1996 (1969).
16. U.S. Mehrota et al, Canod, J. Chem., 48, 1148 (1970)
17. M.C. Agarwal et al, J. Inorg. Nucl. Chem. 32, 125 (1970).
18. U.S. Mehrotra et al, J. Inorg. Nucl. Chem. 32, 2325 (1970)
19. V.K. Jindal et al, J. Chem. Soc., A, 2060 (1970).

20. V.K. Jindal et al, Z. Nat. 256, 188 (1970).

21. V.K. Jindal et al, J. Chem. Soc., A, 622 (1970).

22. S.P. Mushran et al, J. Chem. Soc., B, 1712 (1970).

23. S.P. Mushran and M.C. Agrawal, J. Phys. Chem., 75, 838 (1971).

24. K.C. Gupta et al, Indian J. Chem., 10, 642 (1972).

25. M.C. Agarwal et al, Z. Nat., 27 b, 401 (1972)

26. U.S. Mehrotra et al, J. Indian Chem Soc. 47, 41 (1970)

27. S.P. Mushran et al, Z. Nat., 27 b, 1161 (1978).

28. S.P. Mushran et al, J. Chem Soc., 762 (1973).

29. S.P. Mushran, M.C. Agrawal and R. Sanehi, Z. Phys, Chem., 255, 273 (1974).

30. A.K. Bose and R. Sanehi et al, J. Indian Chem. Soc., 50, 197 (1973).

31. A.K. Bose et al, Indian J. Chem., 11, 896 (1973).

32. R. Sanehi et al, Z. Nat., 28 b, 483 (1973).

33. R. Sanehi et al, Indian J. Chem., 12, 311 (1974).

34. S.P. Mushran et al, Proc. Nat, Acad. Sci. India, 43, 105 (1975).

35. S.P. Mushran et al, J. Indian Chem. Soc., 51, 145 (1975).

36. S.P. Mushran et al, J. Indian Chem. Soc., 51, 433 (1974).

37. R.K. Sharma, A.K. Bose et al, Bull. Acad. Polong. Sci. Ser. Chim. 22, 889 (1974).

38. A. Kumar et al, Montasch. Chem. 106, 863 (1975).

39. A. Kumar et al, J., Indian Chem. Soc. 53, 765 (1976).

40. J. Sharma et al, Indian J. Chem. 19, 475 (1980).

41. J. Sharma et al, Curr. Sci. 48, 629 (1979).

42. A. Berka, Chemic, 10, 121 (1958).

43. S.N. Katgeri et al, Indian J. Chem. 18 A, 29 (1980).

44. M.M. Campbell and G. Johnson, Chem. Rev. 78, 65 (1978).

45. W. Poethke and F. Wolf, Z. Anorg. Allg. Chem., 268, 244 (1952).

46. N.O. Engfeldt, Z. Phys. Chem., 726, 1 (1923).

47. T. Carlsen, Denk. Tidersks, Farm, 30, 29 (1956).

48. R. Dietzel et al, Apoth, Ztg., 44, 1007 (1929).

49. H. Anders, Pharm. Zentralhalle, 92, 198 (1953).

50. E. Bishop & V.J. Jennings, Talanta, 1, 197 (1958).

51. V.R.S. Raw et al, Talanta, 17, 770 (1970).

52. F.G. Mann and W.J. Pope, J. Chem. Soc.,1052 (1922).

53. D. Carr et al, Tetrahedron lett., 477 (1969).

54. F.G. Soper, J. Pope, J. Chem. Soc., 125, 1899 (1924).

55. J.C. Morris, et al, J. Am. Chem. Soc., 70, 2036 (1948).

56. D.S. Mahadevappa, Curr. Sci., 33, 710 (1964).

57. D.S. Mahadevappa, Curr. Sci., 34, 530 (1965).

58. A.S.A. Murthy et al, Curr. Sci., 44, 5 (1975).

59. D.S. Mahadevappa et al, Talanta, 20, 349 (1973).

60. D.S. Mahadevappa et al, Aust. J. Chem., 27, 1203 (1974).

61. D.S. Mahadevappa et al, Curr. Sci. , 45, 216 (1976).

62. D.S. Mahadevappa et al, Indian J. Chem. 13, 976 (1975).

63. J. Caull et al, J. Am. Chem Soc., 57, 1489 (1935).

64. L. J. Reed et al, J. Phys. Chem., 33, 760 (1929).

65. A. Kucsman et al, Tetra Hedron, 18, 75 (1962).

66. G. Modena et al, Gazetta, 87, 1306 (1957).

67. K. Weker and F. Vallic, Z. Phys. Chem. 238, 353 (1968).

68. T. Higuchi and A. Hussain, J. Chem, Soc, B, 549 (1967).

69. M.M. Natarajan et al, J. Chem, Soc, 2, 1590 (1975).

70. J. Sharma, L. Pandey, S.M. Pandey and S.P. Mushran, Proc. Nat. Acad. Sci., 49, (1979).

71. K.K. Banerjee, Indian J. Chem., 16 A, 595 (1978).

72. S. Vivekanand, K. Venkata Rao and M. Santappa, Indian J. Chem., 17 A, 503 (1979).

73. P.S. Radhakrishnamurti and B. Sahu, Indian J. Chem., 17 A, 381 (1979).

CHAPTER II

MATERIALS AND METHOD

2.1 : PREPARATION OF SOLUTIONS

Lobe - Chemie (pronalysis) sample of Chloramine - T (known as sodium salt of N - chloro - para toluenesulphonamide, which is also known as toluene - para - sulphonosodic chloramide) was used in the present investigation as oxidant. Its solution was prepared by dissolving an appropriate amount of its sample in a definite value of doubly distilled water. In order to ensure maximum stability[1] of Chloramine - T solution, it was stored in jena glass bottle coated from outside with black Japan. The strength of the Chloramine - T solution was checked from time to time iodometrically[2] using starch as indicator.

Aqueous solutions of cyclopentanol, cyclohexanol and 2 - methylcyclo hexanal (all E. Merck) were prepared in doubly distilled water by dissolving their desired weighed samples. Standard solution of sodium hydroxide was prepared by dissolving its E.Merck sample in boiled doubly distilled water, and the resulting solution was standardised by standard solution of oxalic acid using phenolphthalein as indicator.

1.0% solution of potassium iodide (E.Merck) was prepared for using it in iodometric titration and 1% starch solution of A.R. (B.D.H.) grade was used as indicator.

Sodium thiosulphate (hypo) solution was prepared by dissolving required amount of its sample (A.R. B.D.H.) in distilled water. Its strength was determined by titrating it against standard solution of copper sulphate iodometrically. Two drops of chloroform was added in hypo solution in order to keep it stable.

Aqueous solution of sodium perchlorate (A.R. Riedel) was prepared in double distilled water in order to use it in maintaining or varying the ionic strength of the medium. The sample of p-toluene sulphonamide (Kotch - light) (England) was dissolved in desired amount of double distilled water.

The solution of osmium tetroxide (Johnson and Matthey) was prepared by dissolving the sample in potassium hydroxide of known strength and the solution was made up to 100 ml in order to keep its concentration at desired level. The strength of the alkali in the solution was noted and was taken into consideration while fixing the concentration of alkali in the reaction mixture.

1.0 N sulphuric acid (A.R.B.D.H.) was prepared by diluting the original concentrated sulphuric acid with desired volume of distilled water. The solution was standardised by titrating it against standard and solution of sodium hydroxide using phenolphthalein as an indicator.

2.2 : METHOD OF INVESTIGATION

The following procedure was followed for investigating the course of reaction :

The reaction mixture containing requisite amounts of chloramine-T alkali and osmium tetroxide were allowed to equilibrate for about half an hour in a waterbath maintained at desired temperature within the range of $\pm 0.1^{0}$c. Appropriate volume of reducing alcohols used here was also brought to the same temperature by placing a separate vessel containing the alcohol in the same water bath. The total initial volume of the reaction mixture was always kept at 100 ml in each case. The progress of the reaction was followed by estimating the remaining concentration of chloramine-T iodometrically 5 ml of aliquot of the reaction mixture was taken out from the reaction bottle and was quickly transferred to a titrating flask containing 5 ml of 1N sulphuric acid and 10% potassium iodide. The remaining amount of chloramine-T liberated an equivalent amount of iodine from the acidified potassium iodide and was titrated against a standard solution of sodium thio-sulphate with starch as indicator. The progress of the reaction was followed by estimating the unconsumed chloramine-T iodometrically at different intervals of time. Kinetics thus followed produced

reproducible results within the range of $\pm 2.8\%$.

In order to determine the order with respect to reactive species, a set of experiments with varying concentrations of particular species is carried out as described above and data at different times are used to calculate the order. This way order of the reaction with all other reactants are determined by the formula described in the following chapters.

2.3 : STOICHIOMETRY

In order to determine the number of equivalents of chloramine-T for the oxidation of molar concentration of reducing cycloalchols, a set of experiments with varying oxidant-reducing alcohol ratios was performed and the remaining amount of chloramine-T was estimated iodometrically. It was observed on the basis of estimations that number of equivalents of chloramine-T required to oxidise 1 Mole of each of reducing cycloalcohol was one. The stoichiometric equations given on the basis of stoichiometric data is expressed as equa. (1-3) for all redox processed studied here.

$$\begin{array}{l} CH_2.CH_2\diagdown \\ | \qquad\qquad\quad CHOH \\ CH_2.CH_2\diagup \end{array} + RNNaCl = \begin{array}{l} CH_2.CH_2\diagdown \\ | \qquad\qquad\quad C{=}O \\ CH_2.CH_2\diagup \end{array} + RNH_2 + NaCl \qquad .....(1)$$

where R stands for $CH_3C_6SO_2$ - group

$$\begin{array}{l} \quad\diagup CH_2.CH_2\diagdown \\ CH_2 \qquad\qquad\qquad CHOH \\ \quad\diagdown CH_2.CH_2\diagup \end{array} + RNNaCl = \begin{array}{l} \quad\diagup CH_2.CH_2\diagdown \\ CH_2 \qquad\qquad\qquad CO \\ \quad\diagdown CH_2.CH_2\diagup \end{array} + RNH_2 + NaCl \qquad .....(2)$$

$$\begin{array}{l} \quad\diagup CH_2CH(CH_3)\diagdown \\ CH_2 \qquad\qquad\qquad\quad CHOH \\ \quad\diagdown CH_2 - CH_2\diagup \end{array} + RNNaCl = \begin{array}{l} \quad\diagup CH_2CH(CH_3)\diagdown \\ CH_2 \qquad\qquad\qquad\quad CO \\ \quad\diagdown CH_2 - CH_2\diagup \end{array} + RNH_2 + NaCl \quad .....(3)$$

The corresponding cycloketones were found as end products.

REFERENCES

1. E. Bishop and V.J. Jennings, Talanta, 1,197(1958)

2. K. Bottger and W. Bottger, Z. Annal. Chemie, 70,225(1927)

CHAPTER III

DEPENDENCE OF THE REACTIONS ON CHLORAMINE-T IN OXIDATION OF CYCLOALCOHOLS CATALYSED BY OSMIUM TETROXIDE IN ALKALINE MEDIA

3 : DEPENDENCE OF THE REACTIONS ON CHLORAMINE-T IN OXIDATION OF CYCLOALCOHOLS CATALYSED BY OSMIUM TETROXIDE IN ALKALINE MEDIA

This chapter deals with the study of determination of order of the reactions with respect to oxidant i.e. chloramine-T in oxidation of a few cycloalcohols such as cyclopentanol, cyclohexanol and 2-methyl cyclohexanol in the presence of alkaline solution of osmium tetroxide. In order to investigate the kinetics with respect to chloramine-T, a set of experiments with varying concentrations of chloramine-T but at fixed concentrations of all other reagents in oxidation of each cycloalcohols under isolation conditions were carried out and the results obtained were presented in the following tables. Tables 1-6, tables 7-12 and tables 13-18 record the kinetic observations obtained in oxidation of cyclopentanol, cyclohexanol and 2- methylcyclohexanol, respectively. The value of k_1 i.e. first-order rate constant was calculated of by the formula $k_1 = (-dc/dt)/[CAT]^*$ where $[CAT]^*$ is the concentration of chloramine-T at which dc/dt was determined. The value of (-dc/dt) i.e. zero-order rate constant was determined from the plot of remaining concentration of chloramine-T and time. The value of $[CAT]^*$ has been given in all tables cyp, cyh and 2-Mcyh have been used for cyclopentanol, cyclohexanol and 2-methylcyclohexanol, respectively in the following tables and elsewhere and CAT is used for chloramine-T.

TABLE 3.1

$[CAT] = 0.80 \times 10^{-3}$ M, $[cyp] = 2.00 \times 10^{-2}$ M,

$[NaOH] = 0.50 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35 ^{o}c

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ Ml^{-1} S^{-1}
0	4.00		
2	3.52		
4	3.18		
8	2.98		
12	2.62		
15	1.88		
20	1.38	0.60	2.48
25	1.04		
30	0.80		
40	0.36		

$k_1 = 4.13 \times 10^{-4}$ sec^{-1}

TABLE 3.2

$[CAT] = 1.00 \times 10^{-3}$ M, $[cyp] = 2.00 \times 10^{-2}$ M

$[NaOH] = 0.50 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35^{0} C

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ $Ml^{-1} S^{-1}$
0	5.00		
2	4.62		
4	4.18		
6	3.78		
8	3.30		
12	2.74		
15	2.02		
20	1.58	0.80	3.46
25	1.24		
30	0.88		
40	0.40		

$k_1 = 4.32 \times 10^{-4}$ sec^{-1}

TABLE 3.3

$[CAT] = 1.25 \times 10^{-3}$ M, $[cyp] = 2.00 \times 10^{-2}$ M,

$[NaOH] = 0.50 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35^{o} c

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ Ml^{-1} S^{-1}
0	6.24		
4	6.16		
8	5.52		
12	5.02		
16	4.30		
20	3.82	1.00	4.22
25	3.02		
30	2.30		
35	1.84		
40	1.50		

$k1 = 4.22 \times 10^{-4}$ sec^{-1}

TABLE 3.4

$[CAT] = 1.67 \times 10^{-3}$ M, $[cyp] = 2.00 \times 10^{-2}$ M

$[NaOH] = 0.50 \times 10^{-2}$, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35° c

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ Ml^{-1} S^{-1}
0	8.32		
5	7.24		
10	6.48		
15	5.50		
20	4.58		
25	3.96	1.38	5.52
30	3.12		
35	2.96		
40	2.04		
45	1.12		

$k1 = 4.00 \times 10^{-4}$ sec^{-1}

TABLE 3.5

$[CAT] = 2.00 \times 10^{-3}$ M, $[cyp] = 2.00 \times 10^{-2}$ M,

$[NaOH] = 0.50 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ $M l^{-1} S^{-1}$
0	10.00		
5	9.40		
10	8.92		
15	8.22		
20	7.62		
25	7.02		
30	6.52	1.80	7.50
40	5.80		
50	5.14		
60	4.58		
70	3.90		

$k1 = 4.17 \times 10^{-4}$ sec^{-1}

TABLE 3.6

[CAT] 4.00×10^{-3} M, [cyp] 2.00×10^{-2} M,
[NaOH] = 0.50×10^{-2} M, [OsO_4] = 1.20×10^{-6} M

Temperature 35^{0} C

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ $M\ell^{-1}$ S^{-1}
0	20.00		
5	18.12		
15	17.06		
30	16.00		
45	15.14		
60	14.08	3.60	15.02
75	13.02		
100	11.00		
125	9.45		
150	8.14		

$k1 = 4.16 \times 10^{-4}$ sec^{-1}

TABLE 3.7

$[CAT] = 0.80 \times 10^{-3}$ M, $[cyh] = 1.00 \times 10^{-2}$ M,

$[NaOH] = 1.25 \times 10^{-2}$ M, $[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature 35°c

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ Ml^{-1} S^{-1}
0	8.32		
5	7.82		
10	7.42		
15	7.18		
25	6.82		
35	6.56	0.7	1.60
60	5.32		
85	4.44		
110	3.04		
140	2.10		
180	1.10		

$k1 = 2.28 \times 10^{-4}$ sec^{-1}

TABLE 3.8

$[CAT] = 1.00 \times 10^{-3}$ M, $[cyh] = 1.00 \times 10^{-2}$ M,

$[NaOH] = 1.25 \times 10^{-2}$ M, $[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature 35^{o} c

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ Ml^{-1} S^{-1}
0	10.36		
5	10.02		
15	9.24		
30	7.98		
45	6.52		
60	5.50		
85	4.40	0.80	1.82
110	3.14		
135	2.56		
165	2.04		

$k1 = 2.27 \times 10^{-4}$ sec^{-1}

TABLE 3.9

$[CAT] = 1.67 \times 10^{-3}$ M, $[cyh] = 1.00 \times 10^{-2}$ M,

$[NaOH] = 1.25 \times 10^{-2}$ M, $[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature 35° c

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ Ml^{-1} S^{-1}
0	8.52		
5	8.18		
10	7.82		
15	7.54		
25	6.52	1.40	3.22
40	5.30		
60	4.04		
80	2.92		
110	1.88		

$k1 = 2.30 \times 10^{-4}$ sec^{-1}

TABLE 3.10

[CAT] = 2.00×10^{-3} M, [cyh] = 1.00×10^{-2} M,

[NaOH] = 1.25×10^{-2} M, [OsO4] = 0.75×10^{-6} M

Temperature 35 ^{o}c

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ Ml^{-1} S^{-1}
0	10.16		
5	10.00		
10	9.76		
20	8.98		
30	8.18		
40	7.16		
50	6.14	1.80	4.00
70	4.56		
90	3.40		
110	2.68		
130	1.98		

$k1 = 2.22 \times 10^{-4}$ sec^{-1}

TABLE 3.11

$[CAT] = 3.00 \times 10^{-3}$ M, $[cyh] = 1.00 \times 10^{-2}$ M,

$[NaOH] = 1.25 \times 10^{-2}$ M, $[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature 35^{o}C

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ $Ml^{-1} S^{-1}$
0	15.20		
5	14.94		
10	14.58		
20	13.46		
30	12.32		
45	9.60	2.80	6.20
60	7.86		
80	5.82		
100	4.66		
140	3.22		

$k1 = 2.21 \times 10^{-4}\ sec^{-1}$

TABLE 3.12

[CAT] 4.50×10^{-3} M, [cyh] 1.00×10^{-2} M,
[NaOH] 1.25×10^{-2} M, [OsO4] 0.75×10^{-7} M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ Ml^{-1} S^{-1}
0	11.40		
5	11.20		
10	10.94		
20	10.06		
30	9.22	4.20	9.20
45	7.24		
60	6.16		
80	5.06		
100	3.48		
130	2.56		
160	1.62		

$k1 = 2.19 \times 10^{-4}$ sec^{-1}

TABLE 3.13

$[CAT] = 0.80 \times 10^{-3}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M,

$[2\text{-Meph}] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 35^{o}C

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ Ml^{-1} S^{-1}
0	5.00		
5	4.86		
10	4.60		
15	4.26		
25	3.70		
35	3.22	0.70	1.21
45	2.86		
60	2.24		
85	1.68		
120	0.92		

$k1 = 1.73 \times 10^{-4}$ sec^{-1}

TABLE 3.14

[CAT] = 1.00×10^{-3} M, [NaOH] = 1.00×10^{-2} M,

[2 Meph] = 1.00×10^{-2} M, [OsO_4] = 0.80×10^{-6} M

Temperature 35 $^{\circ}$C

Time (min)	Volume of hypo solution in ml	[CAT]* $\times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ Ml^{-1} S^{-1}
0	6.24		
5	6.08		
10	5.76		
15	5.32		
25	4.58	0.80	1.42
35	4.00		
45	3.52		
60	2.72		
85	2.18		
120	1.22		

$k1 = 1.78 \times 10^{-4}$ sec^{-1}

TABLE 3.15

$[CAT] = 1.60 \times 10^{-2}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M,

$[2\ Mcyh] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ $Ml^{-1} S^{-1}$
0	10.00		
5	9.72		
10	9.30		
15	8.56		
25	7.48		
35	6.50	1.50	2.68
45	5.68		
60	4.54		
85	3.30		
105	2.38		
130	1.64		

$k1 = 1.78 \times 10^{-4}$ sec^{-1}

TABLE 3.16

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M,

$[2\ Mcyh] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ Ml^{-1} S^{-1}
0	12.50		
5	12.12		
10	11.58		
15	10.68		
25	9.40	1.80	3.22
35	8.14		
45	7.12		
60	5.64		
90	4.22		
120	2.34		

$k1 = 1.78 \times 10^{-4}$ sec^{-1}

TABLE 3.17

$[CAT] = 3.20 \times 10^{-3}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M,

$[2\ Mcyh] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 35^{o}C

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ S^{-1}$
0	10.02		
5	9.68		
10	9.32		
15	8.62		
25	7.52		
35	6.48	3.00	5.20
45	5.72		
60	4.48		
85	3.30		
120	1.82		

$k1 = 1.73 \times 10^{-4}\ sec^{-1}$

<u>TABLE 3.18</u>

$[CAT] = 4.00 \times 10^{-3}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M,

$[2\ Mcyh] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ Ml^{-1} S^{-1}
0	12.48		
5	12.08		
10	11.50		
15	10.64		
25	9.40	3.60	6.22
35	8.08		
45	7.04		
60	5.62		
80	4.36		
100	3.02		

$k1 = 1.72 \times 10^{-4}$ sec^{-1}

The kinetic observations made in tables 3.1-3.6, 3.7-3.12 and 3.13-3.18 have been summarised in tables 3.19, 3.20 and 3.21 respectively.

TABLE 3.19

$[Cyp] = 2.00 \times 10^{-2}$ M, $[NaOH] = 0.50 \times 10^{-2}$ M

$[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35 °C

$[CAT] \times 10^{3}$ M	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ Ml^{-1} S^{-1}	$k1 \times 10^{4}$ sec^{-1}
0.80	0.60	2.48	4.13
1.00	0.80	3.46	4.32
1.25	1.00	4.22	4.22
1.67	1.38	5.52	4.00
2.00	1.80	7.50	4.17
4.00	3.60	15.02	4.16

Average $k1 = 4.16 \times 10^{-4}$ sec^{-1}

TABLE 3.20

[Cyh] 1.00×10^{-2} M, [NaOH] = 1.25×10^{-2} M

[OsO4] = 0.75×10^{-6} M

Temperature 35 °C

$[CAT] \times 10^{3}$ M	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ $Ml^{-1} S^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0.80	0.70	1.60	2.28
1.00	0.80	1.82	2.27
1.67	1.40	3.22	2.30
2.00	1.80	4.00	2.22
3.00	2.80	6.20	2.21
4.50	4.20	9.20	2.19

Average k1 = 2.24×10^{-4} sec^{-1}

TABLE 3.21

$[2\ MCyh] = 1.00 \times 10^{-2}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M

$[OsO_4]$ 0.80×10^{-6} M

Temperature 35 ^{o}C

$[CAT] \times 10^{3}$ M	$[CAT]^{*} \times 10^{3}$ M	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ S^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0.80	0.70	1.21	1.73
1.00	0.80	1.42	1.78
1.60	1.50	2.68	1.78
2.00	1.80	3.22	1.78
3.20	3.00	5.20	1.73
4.00	3.60	6.22	1.72

Average $k1 = 1.75 \times 10^{-4}\ sec^{-1}$

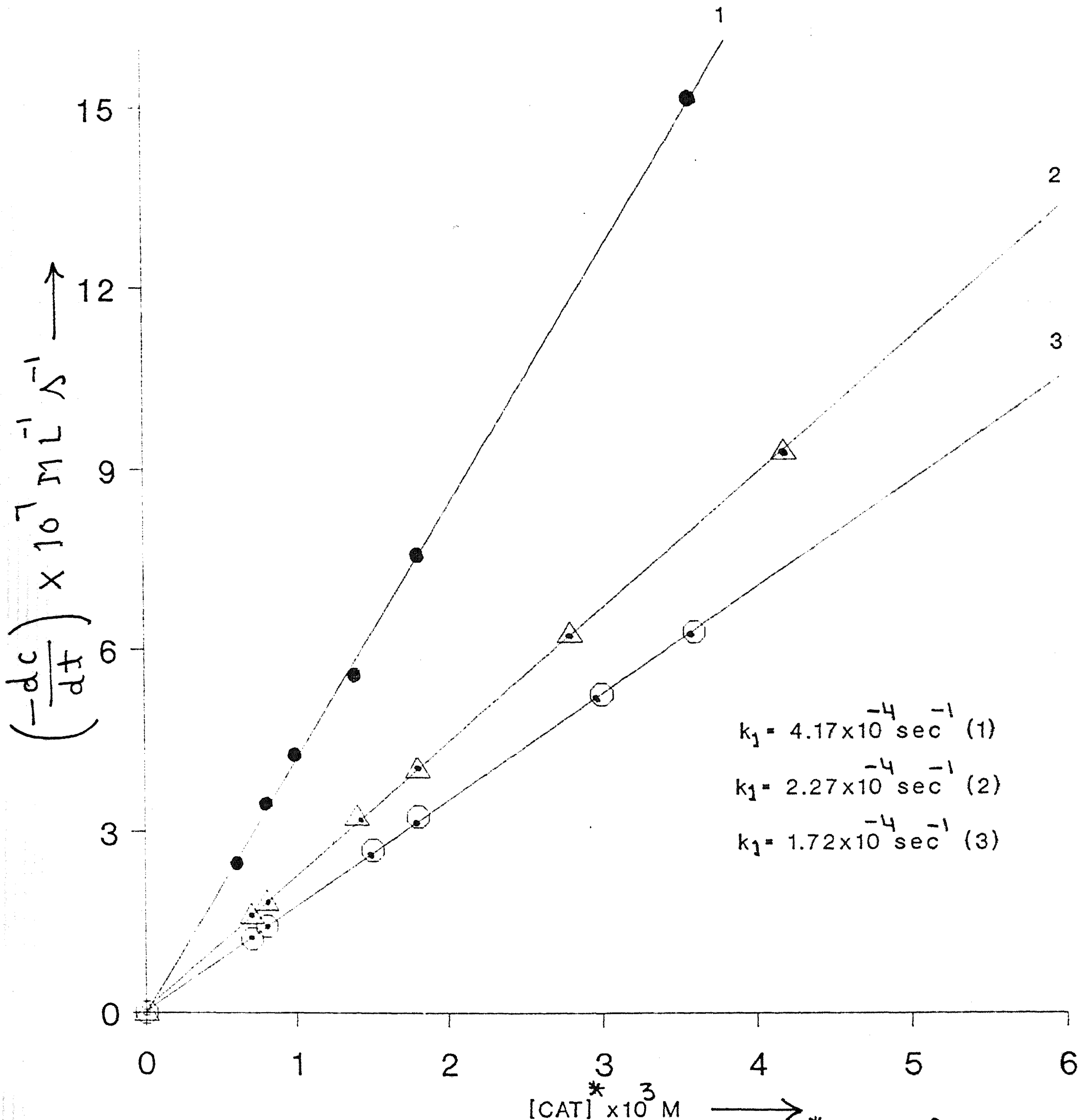


FIG.3.1 : PLOT OF (-dc/dt) Vs. $[CAT]^{*}$ AT 35°C

1. Under the conditions of table 3.19 (cyp)
2. Under the conditions of table 3.20 (cyh)
3. Under the conditions of table 3.21 (2-MCYh)

It is evident from the kinetic results of the summarised tables 3.19 3.21 that k1 values are nearly constant at different concentrations of chloramine T which indicates first order kinetics with respect to chloramine T.

When (-dc/dt) values are plotted against $[CAT]^*$, a straight line in oxidation of each of cycloalcohols is obtained (Fig.3.1). The slope of the straight line gives the value of k1. The graphical k1 value closely resembles with average k1 value given in the bottom of each table. This confirms first-order dependence on Chloramine-T in oxidation of cyclopentanol, cyclohexanol and 2-methyl cyclohexanol.

CHAPTER IV

DEPENDENCE OF THE REACTIONS ON CYCLOALCOHOLS IN THEIR OXIDATION BY CHLORAMINE-T CATALYSED BY ALKALINE SOLUTION OF OSMIUM TETROXIDE

4 : DEPENDENCE OF REACTIONS ON CYCLOALCOHOLS IN THEIR OXIDATION BY CHLORAMINE-T CATALYSED BY ALKALINE SOLUTION OF OSMIUM TETROXIDE.

In this chapter the main aim is to investigate dependence of oxidation of cycloalcohols by Chloramine T on reducing agents in the presence of alkaline solution of osmium tetroxide which is used here as homogeneous catalyst. In order to obtain the aforesaid aim a set of experiments at various concentration of each of cycloalcohols but at fixed concentrations of all other reagents have been performed. Here also the values of k1 and (-dc/dt) have been determined by the method described in 3rd chapter. The results of various experiments have been recorded in tables 4.1-4.5, 4.6-4.10 and 4.11-4.15 in oxidation of cyclopentanol, cyclohexanol and 2-methyl cyclohexanol respectively.

Table 4.1

$[CAT] = 2.00 \times 10^{-3}$ M, $[cyp] = 1.00 \times 10^{-2}$ M

$[NaOH] = 0.50 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35 °C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $ml^{-1}\ s^{-1}$	$k_1 \times 10^{4}$ sec^{-1}
0	10.00		
10	9.46		
20	8.96		
30	8.18		
40	7.52	3.62	2.01
50	6.92		
60	6.42		
80	5.74		
100	5.08		
140	4.52		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M at which (-dc/dt) was determined.

Table 4.2

$[CAT] = 2.00 \times 10^{-3}$ M, $[cyp] = 1.50 \times 10^{-2}$ M

$[NaOH] = 0.50 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ ml^{-1} s^{-1}	$k_1 \times 10^{4}$ sec^{-1}
0	10.00		
10	9.34		
20	8.80		
30	8.00		
40	7.34	5.48	3.05
50	6.72		
60	6.20		
80	5.52		
100	4.88		
140	4.14		

$[CAT]^{*} = 1.80 \times 10^{-3}$ at which (-dc/dt) was determined.

Table 4.3

$[CAT] = 2.00 \times 10^{-3}$ M, $[cyp] = 3.00 \times 10^{-2}$ M

$[NaOH] = 0.50 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35 °C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $ml^{-1}\ s^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
5	9.34		
10	8.86		
15	8.18		
20	7.42		
30	6.44	10.[illegible]	6.09
40	5.64		
50	5.02		
60	4.58		
80	3.72		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M at which (-dc/dt) was determined.

Table 4.4

$[CAT] = 2.00 \times 10^{-3}$ M, $[cyp] = 4.00 \times 10^{-2}$ M

$[NaOH] = 0.50 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
5	9.00		
10	8.16		
15	7.60		
20	7.06	14.82	8.23
25	6.46		
30	5.72		
40	5.20		
50	4.46		
60	3.92		
80	1.88		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M at which (-dc/dt) was determined.

Table 4.5

[CAT] 2.00×10^{-3} M, [cyp] = 5.00×10^{-3} M

[NaOH] 0.50×10^{-2} M, [OsO4] = 1.20×10^{-6} M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
5	8.88		
10	8.02		
15	7.40		
20	6.92	18.92	10.51
25	6.34		
30	5.50		
40	5.02		
50	4.18		
60	3.72		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M at which (-dc/dt) was determined.

Table 4.6

$[CAT] = 2.00 \times 10^{-3}$ M, $[cyh] = 0.50 \times 10^{-2}$ M

$[NaOH] = 1.25 \times 10^{-2}$ M, $[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature 35 °C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $ml^{-1}\ s^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	10.20		
10	9.84		
20	9.72		
30	9.38		
50	8.90	2.00	1.11
60	8.48		
75	8.00		
100	6.42		
125	5.68		
150	4.20		
200	3.52		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M at which (-dc/dt) was determined.

Table 4.7

[CAT] = 2.00×10^{-3} M, [cyh] = 1.50×10^{-2} M

[NaOH] = 1.25×10^{-2} M, [OsO4] = 0.75×10^{-6} M

Temperature 35^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
5	9.80		
10	9.46		
20	8.62		
30	7.88		
40	7.06	6.08	3.38
50	[illegible].00		
60	4.50		
80	3.52		
100	[illegible].00		

$[CAT]^{*}$ = 1.80×10^{-3} M at which (-dc/dt) was determined.

Table 4.8

$[CAT] = 2.00 \times 10^{-3}$ M, $[cyh] = 2.00 \times 10^{-2}$ M

$[NaOH] = 1.25 \times 10^{-2}$ M, $[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.20		
5	9.70		
10	8.98		
20	8.18		
30	7.20		
40	6.10	8.6	4.78
50	5.08		
60	4.34		
80	3.12		
100	2.06		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M at which (-dc/dt) was determined.

Table 4.9

[CAT] = 2.00×10^{-3} M, [cyh] = 2.50×10^{-2} M

[NaOH] = 1.25×10^{-2} M, [OsO_4] = 0.75×10^{-6} M

Temperature 35 °C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $ml^{-1}\ s^{-1}$	$k_1 \times 10^{4}$ sec^{-1}
0	10.20		
5	9.50		
10	8.80		
20	7.94		
30	7.00		
40	5.96	10.82	6.01
50	4.92		
60	4.00		
80	2.96		
100	1.92		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M at which (-dc/dt) was determined.

Table 4.10

$[CAT] = 2.00 \times 10^{-3}$ M, $[cyh] = 3.00 \times 10^{-2}$ M

$[NaOH] = 0.75 \times 10^{-2}$ M, $[OsO_4]^{-} = 0.75 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.20		
5	9.34		
10	8.72		
15	8.18		
20	7.78		
30	6.82		
40	5.84	12.52	6.96
50	4.82		
60	4.00		
80	2.82		
100	1.80		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M at which (-dc/dt) was determined.

Table 4.11

$[CAT] = 2.00 \times 10^{-3}$ M, $[2\text{-mcyh}] = 0.50 \times 10^{-2}$ M

$[NaOH] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 35 °C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
10	12.10		
20	11.60		
30	10.72		
50	9.46		
70	8.20	1.50	0.83
90	7.18		
120	5.62		
150	4.68		
180	3.98		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M at which (-dc/dt) was determined.

Table 4.12

$[CAT] = 2.00 \times 10^{-3}$ M, $[2\text{-mcyh}] = 1.25 \times 10^{-2}$ M

$[NaOH] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $ml^{-1}\ s^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
5	12.00		
10	11.44		
15	10.52		
25	9.20	3.80	2.11
35	7.92		
45	6.94		
60	5.42		
90	3.86		
120	2.78		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M at which (-dc/dt) was determined.

<u>Table 4.13</u>

$[CAT] = 2.00 \times 10^{-3}$ M, $[2\text{-mcyh}] = 1.50 \times 10^{-2}$ M

$[NaOH] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
5	11.80		
10	11.30		
15	10.36		
25	9.00		
35	7.62	4.60	2.55
45	6.60		
60	5.10		
90	3.72		
120	2.60		
140	1.86		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M at which (-dc/dt) was determined.

Table 4.14

[CAT] = 2.00×10^{-3} M, [2 Mcyh] = 2.00×10^{-2} M

[NaOH] = 1.00×10^{-2} M, [OsO4] = 0.80×10^{-6} M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
5	11.24		
10	10.46		
15	9.14		
25	8.02	5.62	3.12
35	6.78		
45	5.42		
60	4.12		
90	2.94		
120	1.98		

$[CAT]^{*}$ = 1.80×10^{-3} M at which (-dc/dt) was determined.

Table 4.15

$[CAT] = 2.00 \times 10^{-3}$ M, $[2\text{-Meyh}] = 2.50 \times 10^{-2}$ M

$[NaOH] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
5	10.86		
10	9.42		
15	8.02		
20	6.56		
25	5.16	7.42	4.12
30	4.08		
35	2.90		
40	2.02		
50	1.46		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M at which (-dc/dt) was determined.

The kinetic data reported in tables 4.1-4.5 & tables 3.5, tables 4.6-4.10 & table 3.10 and tables 4.11-4.15 & table 3.16 have been summariced in table 4.16, 4.17 and 4.18, respectively.

Table 4.16

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 0.50 \times 10^{-2}$ M

$[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35^{o} C

$[cyp] \times 10^{2}$ M	$(-dc/dt) \times 10^{7}$ ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}	10^{2} $k2=k1/[cyp]$ m^{-1} sec^{-1}
1.00	3.62	2.01	2.01
1.50	5.48	3.05	2.03
2.00	7.50	4.17	2.08
3.00	10.96	6.09	2.03
4.00	14.82	8.23	2.06
5.00	18.92	10.51	2.10

$[CAT]^{*} = 1.80 \times 10^{-3}$ M,

Average $k2 = 2.05 \times 10^{-2}$ M^{-1} L sec^{-1}

Table 4.17

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.25 \times 10^{-2}$ M

$[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature $35\,^{o}C$

$[cyh] \times 10^{2}$ M	$(-dc/dt) \times 10^{7}$ $ml^{-1}\ s^{-1}$	$k1 \times 10^{4}$ sec^{-1}	$10^{2}\ k_{2} = k1/[cyh]$ $m^{-1}\ \ell\ sec^{-1}$
0.50	2.00	1.11	2.22
1.00	4.00	2.22	2.22
1.50	6:00	3.38	2.25
2.00	8.60	4.78	2.39
2.50	10.82	6.01	2.40
3.00	12.52	6.94	2.31

$[CAT]^{*} = 1.80 \times 10^{-3}$ M

Average $k2 = 2.29 \times 10^{-2}\ M^{-1}\ L\ sec^{-1}$

Table 4.18

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M

$[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature $35^{o}C$

$[2\text{-mcyh}] \times 10^{2}$ M	$(-dc/dt) \times 10^{7}$ $ml^{-1}\ s^{-1}$	$k1 \times 10^{4}$ sec^{-1}	$10^{2}\ k2 = k1/[2\text{-mcyh}]$ $M^{-1}\ lsec^{-1}$
0.50	1.50	0.83	1.66
1.00	3.22	1.78	1.78
1.25	3.80	2.11	1.69
1.50	4.60	2.55	1.70
2.00	5.62	3.12	1.56
2.50	7.42	4.12	1.64

$[CAT]^{*} = 1.80 \times 10^{-3}$ M

Average $k2 = 1.67 \times 10^{-2}\ M^{-1}\ L\ sec^{-1}$

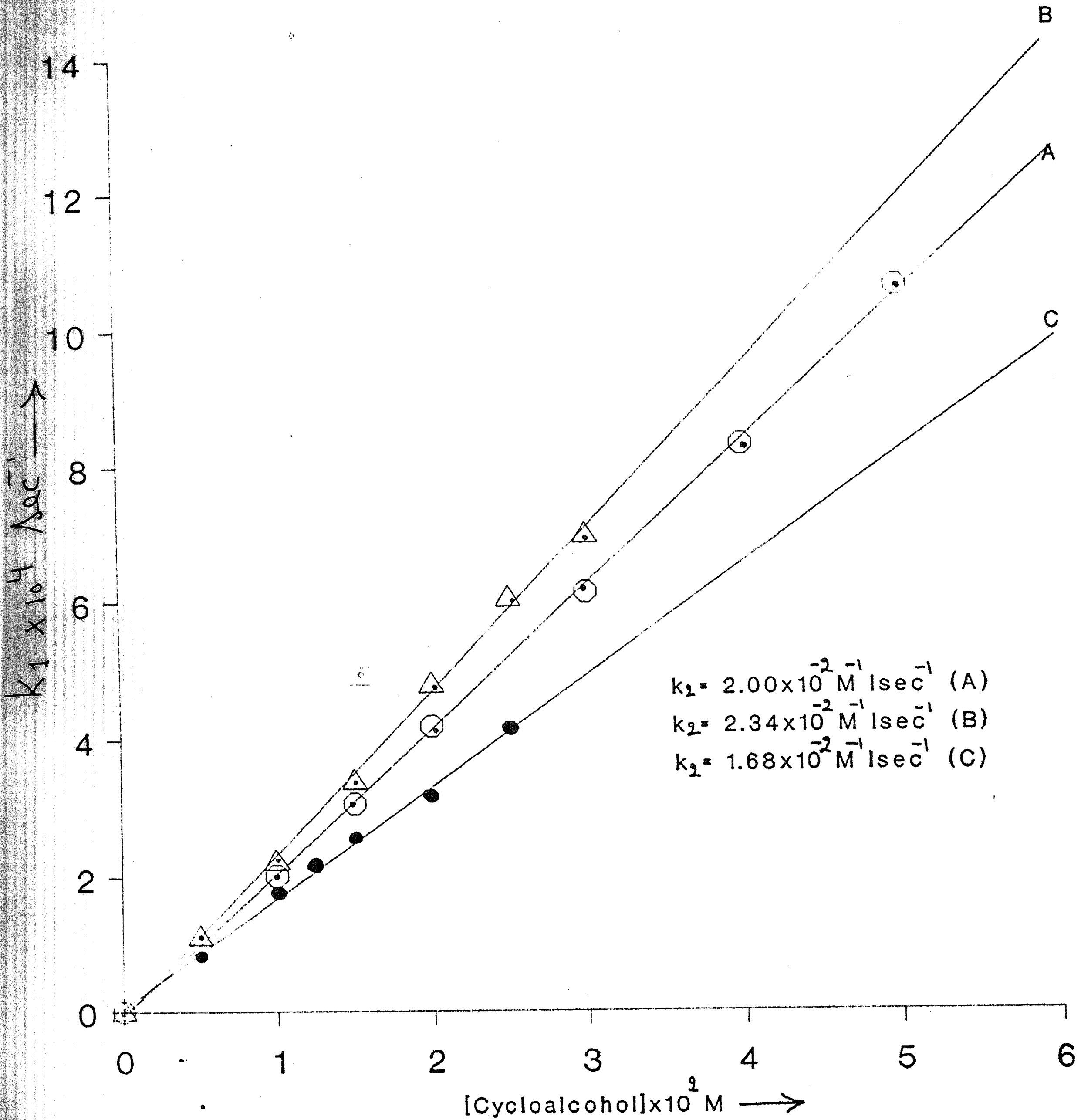


FIG.4.1 : PLOT OF k_1 Vs. [CYCLOALCOHOLS] AT 35°C
(A) : Under the conditions of table 4.16 (cyp)
(B) : Under the conditions of table 4.17 (cyh)
(C) : Under the conditions of table 4.18 (2-MCYh)

Careful examination of data of summarised tables 4.16, 4.17 and 4.18 clearly indicates that first order rate constant i.e. k1 increases linearly with increase in concentration of cycloalcohol, showing thus first-order dependence on each of cycloalcohol. Practically and nearly constant valves of k2 i.e. second order rate constant obtained at different concentrations of each of cycloalcohol also confirm first-order kinetics with respect to reducing cycloalcohols.

When k1 values are plotted against concentration of cycloalcohol in each case, a straight line passing through origin is obtained (Fig.4.1), The slope of the straight lines gives the value of k2. Thus graphical k2 value has been found to be closer to average k2 valve given in each summarised tables. The closeness in k2 valves obtained graphically and by calculation confirms first order in each of reducing cycloalcohol.

CHAPTER V

DEPENDENCE OF REACTIONS ON SODIUM HYDROXIDE IN OXIDATION OF CYCLOALCOHOLS BY CHLORAMINE-T CATALYSED BY ALKALINE SOLUTION OF OSMIUM TETROXIDE

5 : DEPENDENCE OF REACTIONS ON SODIUM HYDROXIDE IN OXIDATION OF CYCLOALCOHOLS BY CHLORAMINE-T CATALYSED BY ALKALINE SOLUTION OF OSMIUM TETROXIDE

This Chapter describes the method adopted for determining order of the reactions with respect to sodium hydroxide in osmium tetroxide catalysed oxidation of cycloalcohols by Chloramine-T. In order to achieve the above aim, a few experiments were carried out in which concentrations of sodium hydroxide were varied at fixed concentrations of all other reagents in oxidation of each cycloalcohol. The results of such experiments were recorded in tables 5.1 - 5.5, 5.6 - 5.10 and 5.11 - 5.15 in oxidation of cyclopentanol, cyclohexanol and 2-methylcyclohexanol respectively. Here also (-dc/dt) and k1 valves have been calculated by procedure given in 3rd chapter value of (-dc/dt) has been determined in all experiments at 1.80×10^{-3} M of chloramine-T concentration which is earlier designated as $[CAT]^*$.

Table 5.1

[CAT] = 2.00×10^{-3} M, [NaOH] = 0.20×10^{-2} M

[Cyp] = 2.00×10^{-2} M, [OsO4] = 1.20×10^{-6} M

Temperature 35 $^{\circ}$C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1} s^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
10	9.46		
20	8.92		
30	8.28		
40	7.66		
50	6.88		
60	6.52		
80	5.84	2.92	1.62
100	5.10		
120	4.52		
150	3.58		

$k2 = k1 / [NaOH] = 8.10 \times 10^{-2}\ M^{-1}\ l\ sec^{-1}$

Table 5.2

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 0.40 \times 10^{-2}$ M

$[Cyp] = 2.00 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
10	9.30		
20	8.62		
30	8.12		
40	7.52	5.74	3.18
50	6.54		
60	6.00		
80	5.44		
100	4.74		
120	4.02		

$k2 = k1 / [NaOH] = 7.95 \times 10^{-2}$ M^{-1} l sec^{-1}

<u>Table 5.3</u>

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M

$[Cyp] = 2.00 \times 10^{-2}$ M, $[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
5	9.00		
10	7.94		
15	6.76		
20	5.64	14.40	8.00
25	4.70		
30	3.72		
35	2.86		
40	2.10		

$k2 = k1 / [NaOH] = 8.00 \times 10^{-2}$ M^{-1} l sec^{-1}

Table 5.4

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.50 \times 10^{-2}$ M

$[Cyp] = 2.00 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
5	8.82		
10	7.84		
15	6.60		
20	5.50	23.00	12.78
25	4.52		
30	3.48		
35	2.68		
40	1.92		
50	1.54		
60	1.00		

$k2 = k1 / [NaOH] = 8.52 \times 10^{-2}$ M^{-1} l sec^{-1}

Table 5.5

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 2.00 \times 10^{-2}$ M

$[Cyp] = 2.00 \times 10^{-2}$ M, $[OsO_4] = 1.00 \times 10^{-6}$ M

Temperature 35°C

ne in)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $ml^{-1}\ s^{-1}$	$k1 \times 10^{4}$ sec^{-1}
	10.00		
	8.60		
	7.70		
	6.42		
	5.34		
	4.40	30.[illegible]	16.67
	3.42		
	2.60		
	1.[illegible]		
	1.42		

$= k1 / [NaOH] = 8.34 \times 10^{-2}\ M^{-1}\ sec^{-1}$

Table 5.6

$[CAT] = 2.00 \times 10^{-3}$ M, [illegible] $= $ [illegible]$.50 \times 10^{-2}$ M

$[Cyh] = 1.00 \times 10^{-2}$ M, [illegible] $= $ [illegible]$.75 \times 10^{-6}$ M

Temperature 35 °C

ne in)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ ml^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.14		
[illegible]	[illegible].86		
[illegible]	9.20		
[illegible]	[illegible]		
[illegible]	[illegible]	1.60	[illegible].89
[illegible]	7.[illegible]		
75	[illegible]40		
00	4.02		
25	3.02		
50	[illegible]		

k2 = k1 / [NaOH] = 1.98×10^{-2} M^{-1} l sec^{-1}

Table 5.7

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M

$[Cyh] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ M l^{-1} s^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.16		
10	9.82		
20	9.00		
30	8.52		
40	8.00		
50	7.44	3.31	1.84
75	5.30		
100	3.86		
125	2.90		
150	2.00		

$k2 = k1 / [NaOH] = 1.84 \times 10^{-2}$ M^{-1} l sec^{-1}

Table 5.8

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.50 \times 10^{-2}$ M

$[Cyh] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature 35 ^{o}C

ime (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ s^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	10.14		
5	9.92		
10	9.60		
20	8.72		
30	7.86	7.94	2.80
45	6.14		
60	4.56		
90	3.22		
120	2.82		

$k2 = k1 / [NaOH] = 1.86 \times 10^{-2}\ M^{-1}\ l\ sec^{-1}$

Table 5.9

$[CAT] = 2.00 \times 10^{-3}\ M$, $[NaOH] = 2.00 \times 10^{-2}\ M$

$[Cyh] = 1.00 \times 10^{-2}\ M$, $[OsO_4] = 0.75 \times 10^{-6}\ M$

Temperature $35^{o}C$

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ s^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	10.14		
5	8.86		
10	9.40		
20	8.50		
30	7.62		
40	6.48	6.62	3.68
60	4.32		
80	3.00		
100	2.44		
120	1.88		

$k2 = k1 / [NaOH] = 1.84 \times 10^{-2}\ M^{-1}\ l\ sec^{-1}$

Table 5.10

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 2.50 \times 10^{-2}$ M

$[Cyh] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature 35^{o} C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ s^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	10.14		
5	9.80		
10	9.26		
20	8.40		
30	7.52	8.56	4.75
40	6.34		
60	4.26		
90	2.86		
110	1.72		

$k2 = 1.90 \times 10^{-2}\ M^{-1}\ 1\ sec^{-1}$

TABLE 5.11

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 0.50 \times 10^{-2}$ M

$[2\text{-Mcyh}] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 35^{o} C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	12.40		
10	12.12		
20	11.64		
30	10.72		
40	10.12	1.40	0.78
50	9.46		
70	8.14		
90	7.18		
120	5.56		
160	4.12		

$k2 = k1 / [NaOH] = 1.56 \times 10^{-2}$ M^{-1} l sec^{-1}

TABLE 5.12

$[CAT] = 2.00 \times 10^{-3}\ M$, $[NaOH] = 1.50 \times 10^{-2}\ M$

$[2\text{-Mcyh}] = 1.00 \times 10^{-2}\ M$, $[OsO_4] = 0.80 \times 10^{-6}\ M$

Temperature $35^{\circ}C$

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ sec^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
5	11.80		
10	11.26		
15	10.28		
25	9.00		
35	7.56	4.51	2.51
45	6.42		
60	5.02		
90	3.66		
120	2.56		

$k2 = k1 / [NaOH] = 1.67 \times 10^{-2}\ M^{-1}\ l\ sec^{-1}$

TABLE 5.13

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 2.00 \times 10^{-2}$ M

$[2\ Mcyh] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ sec^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
5	11.20		
10	10.42		
15	9.00		
20	8.12		
25	7.26	5.80	3.22
35	6.50		
45	5.38		
60	4.00		
80	2.96		

$k2 = k1 / [NaOH] = 1.61 \times 10^{-2}\ M^{-1}\ 1\ sec^{-1}$

<u>TABLE 5.14</u>

[CAT] = 2.00×10^{-3} M, [NaOH] = 2.50×10^{-2} M

[2-Me[illegible]] = 1.00×10^{-2} M, [OsO_4] = 0.80×10^{-6} M

Temperature 35°C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
5	10.88		
10	9.38		
15	8.00		
20	6.48		
25	5.00	7.62	4.23
30	4.02		
40	2.14		
50	1.70		
60	1.52		

$k2 = k1 / [NaOH] = 1.69 \times 10^{-2}$ M^{-1} l sec^{-1}

TABLE 5.15

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 3.00 \times 10^{-2}$ M

$[2\text{-Mcyh}] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 35 $^{\circ}$C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $M1^{-1}$ sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
5	10.62		
10	9.16		
15	7.78		
20	6.02	9.21	5.12
25	4.88		
30	3.78		
35	2.80		
40	1.90		

$k2 = k1 / [NaOH] = 1.70 \times 10^{-2}$ M^{-1} $1\ sec^{-1}$

The kinetic results recorded in tables 5.1-5.5 & table 3.5, tables 5.6-5.10 & table 3.10 and tables 5.11-5.15 & table 3.16 have been summarised in tables 5.16, 5.17 and 5.18 respectively.

TABLE 5.16

$[CAT] = 2.00 \times 10^{-3}$ M; $[cyp] = 2.00 \times 10^{-2}$ M

$[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35°C

$[NaOH] \times 10^{2}$ M	$k_1 \times 10^{4}$ sec^{-1}	$10^{2}\ k_2 = k_1/[NaOH]$ M^{-1} l sec^{-1}
0.20	1.62	8.10
0.40	3.18	7.95
0.50	4.17	8.30
1.00	8.00	8.00
1.50	12.78	8.52
2.00	16.67	8.34

Average $k_2 = 8.21 \times 10^{-2}$ M^{-1} l sec^{-1}

TABLE 5.17

$[CAT] = 2.00 \times 10^{-3}$ M, $[cyh] = 1.00 \times 10^{-2}$ M

$[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature 35°C

$[NaOH] \times 10^{2}$ M	$k1 \times 10^{4}$ sec^{-1}	10^{2} $k2 = k1/[NaOH]$ M^{-1} l sec^{-1}
0.50	0.89	[illegible]
1.00	1.84	1.84
1.25	2.22	1.78
1.50	2.80	1.86
2.00	3.68	1.84
2.50	4.75	1.90

Average $k2 = 1.86 \times 10^{-2}$ M^{-1} l sec^{-1}

<u>TABLE 5.18</u>

$[CAT] = 2.00 \times 10^{-3}$ M, [2 Meyh] $= 1.00 \times 10^{-2}$ M .

$[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 35 $^{\circ}$C

$[NaOH] \times 10^{2}$ M	$k_1 \times 10^{4}$ sec^{-1}	$10^{2}\ k_2 = k_1/[NaOH]$ M^{-1} l sec^{-1}
0.50	0.78	1.56
1.00	1.79	1.79
1.50	2.51	1.67
2.00	3.22	1.61
2.50	4.23	1.69
3.00	5.12	1.70

Average $k_2 = 1.67 \times 10^{-2}$ M^{-1} l sec^{-1}

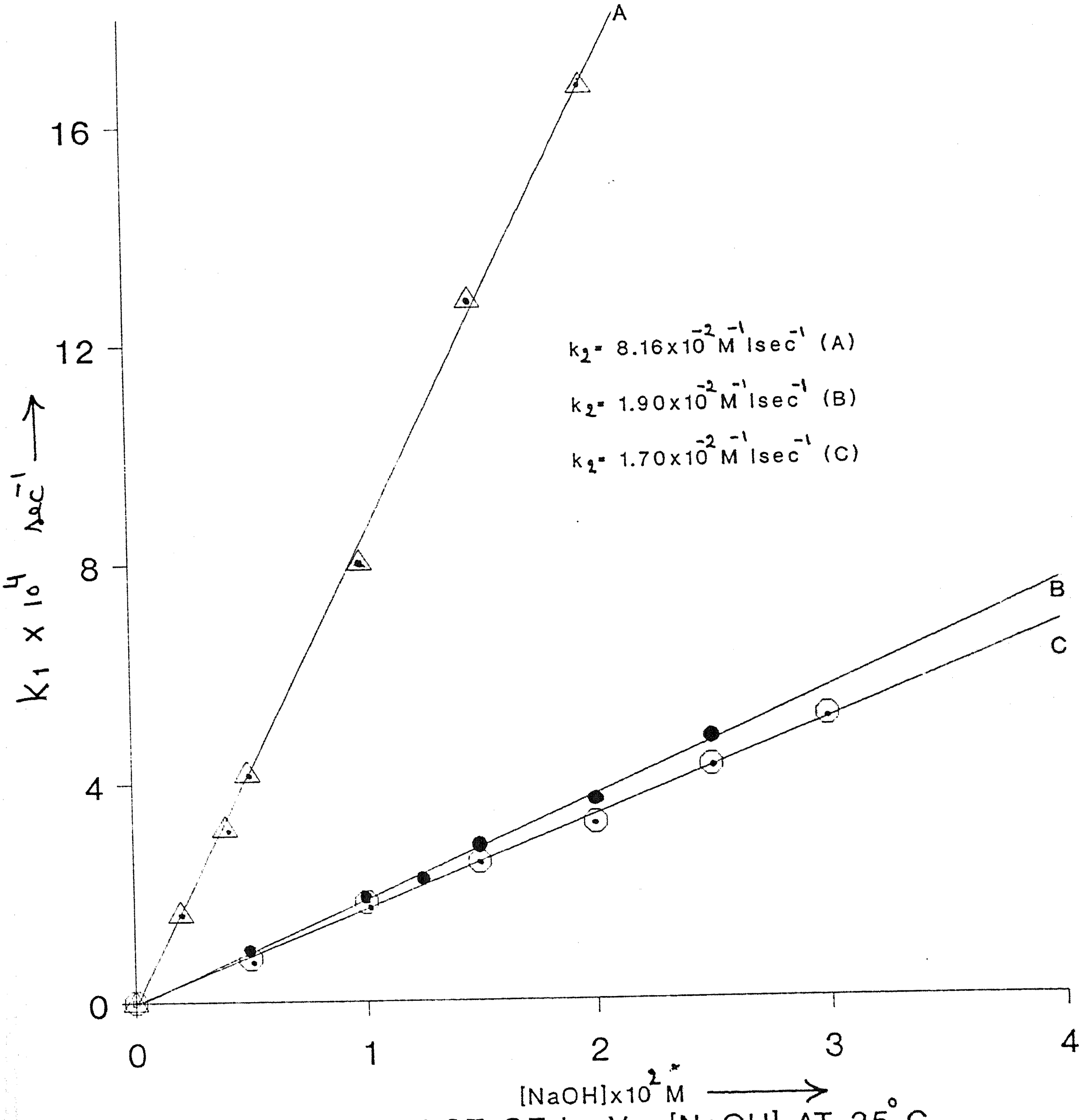


FIG.5.1 : PLOT OF k Vs. [NaOH] AT 35°C
(A) : Under the conditions of table 5.16
(B) : Under the conditions of table 5.17
(C) : Under the conditions of table 5.18

It is quite obvious from the results recorded in summarised tables 5.16, 5.17 and 5.18 that on increasing the concentration of sodium hydroxide in oxidation of each cycloalcohol, the first order velocity constant i.e. k1 value increases linearly showing first order dependence on sodium hydroxide concentration. The near constant k2 values at different concentrations of sodium hydroxide further supports the conclusion that the reaction is first-order with respect to sodium hydroxide.

On plotting k1 values against [NaOH] in oxidation of each cycloalcohols, a straight line with slope(Fig 5.1) equal to k2 is obtained. The value of slope i.e. k2 as graphically obtained agrees well with average k2 value recorded in summarised table correspondingly. The fair degree of closeness in k2 values obtained by calculation and graphically, further confirms first-order kinetics with respect to sodium hydroxide.

CHAPTER VI

DEPENDENCE OF THE REACTIONS ON OSMIUM TETROXIDE IN OXIDATION OF CYCLOALCOHOLS BY ALKALINE CHLORAMINE-T SOLUTION

6 : DEPENDENCE OF REACTIONS ON OSMIUM TETROXIDE IN OXIDATION OF CYCLOALCOHOLS BY ALKALINE CHLORAMINE-T SOLUTION

In this chapter, an attempt has been made to investigate the dependence of oxidation-action of cycloalcohols by alkaline chloramine-T solution on osmium tetroxide which has been used here as homogeneous catalyst, For this purpose a number of experiments with varying concentrations of osmium tetroxide at fixed concentrations of all other reagents have been carried out and the results of such experiments have been given in tables 6.1-6.5, 6.6-6.10 and 6.11-6.15 in oxidation of cyclopentanol, cyclohexanol and 2-methyl-cyclohexanol respectively. Here (-dc/dt), k1 and k2 values have been calculated by the same procedure as described in previous chapters. In each experiment the value of $[CAT]^*$ has been kept 1.80×10^{-3} M at which (-dc/dt) has been determined.

TABLE 6.1

[CAT] = 2.00×10^{-3} M, [NaOH] = 0.50×10^{-2} M

[cyp] = 2.00×10^{-2} M, [OsO4] = 0.30×10^{-6} M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ sec^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
10	9.46		
20	9.00		
30	8.42		
40	7.80	2.02	1.12
50	7.24		
60	6.76		
80	6.12		
100	5.36		
125	4.76		
150	4.26		

$k2 = k1 / [OsO4] = 3.73 \times 10^{2}\ M^{-1}\ l\ sec^{-1}$

TABLE 6.2

$[CAT] = 2.00 \times 10^{-3}\ M$, $[NaOH] = 2.50 \times 10^{-2}\ M$

$[cyp] = 2.00 \times 10^{-2}\ M$, $[OsO_4] = 0.60 \times 10^{-6}\ M$

Temperature $35\ ^{\circ}C$

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ sec^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
10	9.40		
20	8.90		
30	8.30		
40	7.62		
50	7.08	3.82	2.12
60	6.52		
80	5.90		
100	5.20		
120	4.58		
140	3.96		

$k2 = 3.53 \times 10^{2}\ M^{-1}\ l\ sec^{-1}$

TABLE 6.3

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 0.50 \times 10^{-2}$ M

$[cyp] = 2.00 \times 10^{-2}$ M, $[OsO_4] = 0.90 \times 10^{-6}$ M

Temperature 35 $^{\circ}$C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ sec^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
5	9.60		
10	9.08		
15	8.46		
20	8.00		
25	7.42	5.52	3.07
35	6.80		
50	5.00		
75	4.12		
100	3.86		

$k2 = 3.41 \times 10^{2}\ M^{-1}\ l\ sec^{-1}$

TABLE 6.4

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 0.50 \times 10^{-2}$ M

[illegible] $= 2.00 \times 10^{-2}$ M, $[OsO_4] = 1.80 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ sec^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
5	9.32		
10	8.70		
15	8.00		
20	7.46		
25	6.82	10.80	6.00
30	6.26		
40	5.62		
50	4.98		
60	4.26		
75	3.12		

$k2 = 3.33 \times 10^{2}\ M^{-1}\ l\ sec^{-1}$

TABLE 6.5

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 0.50 \times 10^{-2}$ M

$[cyp] = 2.00 \times 10^{-2}$ M, $[OsO_4] = 2.40 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
5	9.20		
10	8.58		
15	7.88		
20	7.16	14.62	8.12
25	6.74		
30	6.[illegible]		
40	5.40		
50	4.68		
60	4.00		

$k2 = 3.38 \times 10^{2}$ M^{-1} $1\ sec^{-1}$

TABLE 6.6

[CAT] = 2.00×10^{-3} M, [NaOH] = 1.25×10^{-2} M

[cyh] = 1.00×10^{-2} M, [OsO4] = 1.00×10^{-6} M

Temperature 35 °C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.14		
5	9.90		
10	9.70		
20	8.80		
30	8.00		
45	6.20	5.60	3.11
60	4.62		
90	3.26		
120	2.26		
150	1.62		

$k2 = 3.11 \times 10^{2}$ M^{-1} 1 sec^{-1}

TABLE 6.7

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.25 \times 10^{-2}$ M

$[cyh] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 1.50 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.14		
5	9.80		
10	9.60		
20	8.62		
30	7.82	8.60	4.78
45	6.00		
60	4.50		
90	[illegible]		
120	2.10		
150	1.28		

$k2 = 3.18 \times 10^{2}$ M^{-1} l sec^{-1}

TABLE 6.8

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.25 \times 10^{-2}$ M

$[cyh] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 2.25 \times 10^{-6}$ M

Temperature 35^{o} C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ sec^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	10.14		
5	9.68		
10	9.26		
20	8.20		
30	7.26		
45	5.46	12.40	6.89
60	4.00		
90	2.80		
120	1.82		
150	0.98		

$k2 = 3.06 \times 10^{2}\ M^{-1}\ l\ sec^{-1}$

TABLE 6.9

[illegible] = 2.[illegible] X 10^{-2} M, [NaOH] = 1.25 X 10^{-2} M

[cyh] = 1.00 X 10^{-2} M, [OsO_4] = 3.00 X 10^{-6} M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	(-dc/dt) X 10^{7} Ml^{-1} sec^{-1}	k1 X 10^{4} sec^{-1}
0	10.1[illegible]		
5	[illegible]		
10	9.0[illegible]		
20	7.46		
30	6.90	16.04	8.91
45	5.00		
60	3.76		
90	2.28		
120	1.50		
150	1.02		

k2 = 2.97 X 10^{2} M^{-1} 1 sec^{-1}

<u>TABLE 6.10</u>

[CAT] = 2.00 X 10^{-3} M, [NaOH] = 1.25 X 10^{-2} M

[[illegible]] = 1.00 X 10^{-2} M, [OsO_4] = 3.75 X 10^{-6} M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	(-dc/dt) X 10^{7} Ml^{-1} sec^{-1}	k1 X 10^{4} sec^{-1}
0	[illegible]		
5	[illegible]		
10	[illegible]		
20	7.66		
30	6.94	21.24	11.78
40	5.[illegible]2		
50	3.92		
60	3.42		
80	2.32		
100	1.84		

Average k2 = 3.14 X 10^{2} M^{-1} sec^{-1}

<u>TABLE 6.11</u>

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M

$[2\text{-Meph}] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.40 \times 10^{-6}$ M

Temperature 35^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ sec^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
10	[illegible]		
20	11.72		
30	10.76		
50	9.48	1.42	0.78
70	8.20		
90	7.[illegible]		
120	5.58		
160	4.12		
200	3.00		

$k2 = k1 / [OsO_4] = 1.95 \times 10^{2}\ M^{-1}\ l\ sec^{-1}$

TABLE 6.12

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M

$[2\text{-Meyh}] = 1.00 \times 10^{-2}$ M, $[OsO_4]$ 1.20×10^{-6} M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
5	11.82		
10	11.26		
15	10.40		
25	9.06	4.42	2.45
35	7.58		
45	6.42		
60	4.98		
90	3.64		
120	2.62		

$k2 = 2.04 \times 10^{2}$ M^{-1} l sec^{-1}

TABLE 6.13

[CAT] = 2.00×10^{-3} M, [NaOH] = 1.00×10^{-2} M

[2 Meph] = 1.00×10^{-2} M, [OsO4] = 1.60×10^{-6} M

Temperature 35 °C

Time (Min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ sec^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
5	11.26		
10	10.50		
15	9.08		
25	8.02	5.72	3.18
35	6.62		
45	5.24		
60	3.96		
90	2.86		
120	1.80		

$k2 = 1.98 \times 10^{2}\ M^{-1}\ l\ sec^{-1}$

TABLE 6.14

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M

$[2\ Mepyh] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 2.00 \times 10^{-6}$ M

Temperature 35 ^{o}C

Time (min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ $Ml^{-1}\ sec^{-1}$	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
5	10.82		
10	9.34		
15	8.00		
20	6.52	7.54	4.19
25	5.10		
30	4.00		
35	[illegible]		
40	2.02		
50	1.08		

$k2 = 2.09 \times 10^{2}\ M^{-1}\ l\ sec^{-1}$

<u>TABLE 6.15</u>

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M

$[2\text{-Mcyh}] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 2.50 \times 10^{-6}$ M

Temperature 35^{o} C

Time (Min)	Volume of hypo solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	12.50		
5	10.56		
10	9.12		
15	7.72		
20	6.00		
25	4.90	9.06	5.03
30	3.80		
35	3.00		
40	1.90		
45	1.06		

$k2 = 2.01 \times 10^{2}$ M^{-1} 1 sec^{-1}

The kinetic data of tables 6.1–6.5 and 3.5, tables 6.6–6.10 and [illegible], and tables 6.11–6.15 and [illegible] have been summarised in tables 6.16, 6.17 and 6.18 respectively.

TABLE 6.16

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 0.50 \times 10^{-2}$ M

$[cyp] = 2.00 \times 10^{-2}$ M

Temperature 35^{o}C

$[OsO_4] \times 10^{6}$ M	$k_1 \times 10^{4}$ sec^{-1}	$k_2 \times 10^{-2}$ M^{-1}
0.30	1.12	3.72
0.60	2.12	3.53
0.90	3.07	3.41
1.20	4.17	3.47
1.80	6.00	3.33
2.40	8.12	3.38

Average $k_2 = 3.47 \times 10^{2}$ M^{-1} 1 sec^{-1}

<u>TABLE 6.17</u>

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.25 \times 10^{-2}$ M

$[cyh] = 1.00 \times 10^{-2}$ M

Temperature 35 ^{o}C

$[OsO_4] \times 10^{6}$ M	$k_1 \times 10^{4}$ sec^{-1}	$k_2 \times 10^{-2}$ M^{-1} l sec^{-1}
0.75	2.22	2.96
1.00	3.11	3.11
1.50	4.78	3.18
2.25	6.89	3.06
3.00	8.91	2.97
3.75	11.78	3.14

Average $k_2 = 3.07 \times 10^{2}$ M^{-1} l sec^{-1}

TABLE 6.18

$[CAT] = 2.00 \times 10^{-3}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M

$[2\text{-Mcyh}] = 1.00 \times 10^{-2}$ M

Temperature 35 $^{\circ}$C

$[OsO_4] \times 10^{6}$ M	$k_1 \times 10^{4}$ sec^{-1}	$k_2 \times 10^{-2}$ M^{-1} l sec^{-1}
0.40	0.78	1.95
0.80	1.78	2.22
1.20	2.45	2.04
1.60	3.18	1.98
2.00	4.19	2.09
2.50	5.02	2.01

Average $k_2 = 2.05 \times 10^{2}$ M^{-1} l sec^{-1}

A close examination of kinetic data reported in summarised tables clearly indicates that k1 values in oxidation of each cycloalcohols used here linearly increases with increase in the concentration of corresponding osmium tetroxide, which shows that order of the reactions is one with respect to osmium tetroxide. First order dependence on osmium tetroxide is also evident from near constant values of k2 reported in each summarised tables.

A plot of k1 vs. [OsO_4] in oxidation of each cycloalcohol yields a straight line passing through origin (Fig. 6.1). The slope of the straight line in each case closely resembles with corresponding average k2 value given in the bottom of each summarised tables. This further, proves and confirms first order kinetics in osmium tetroxide.

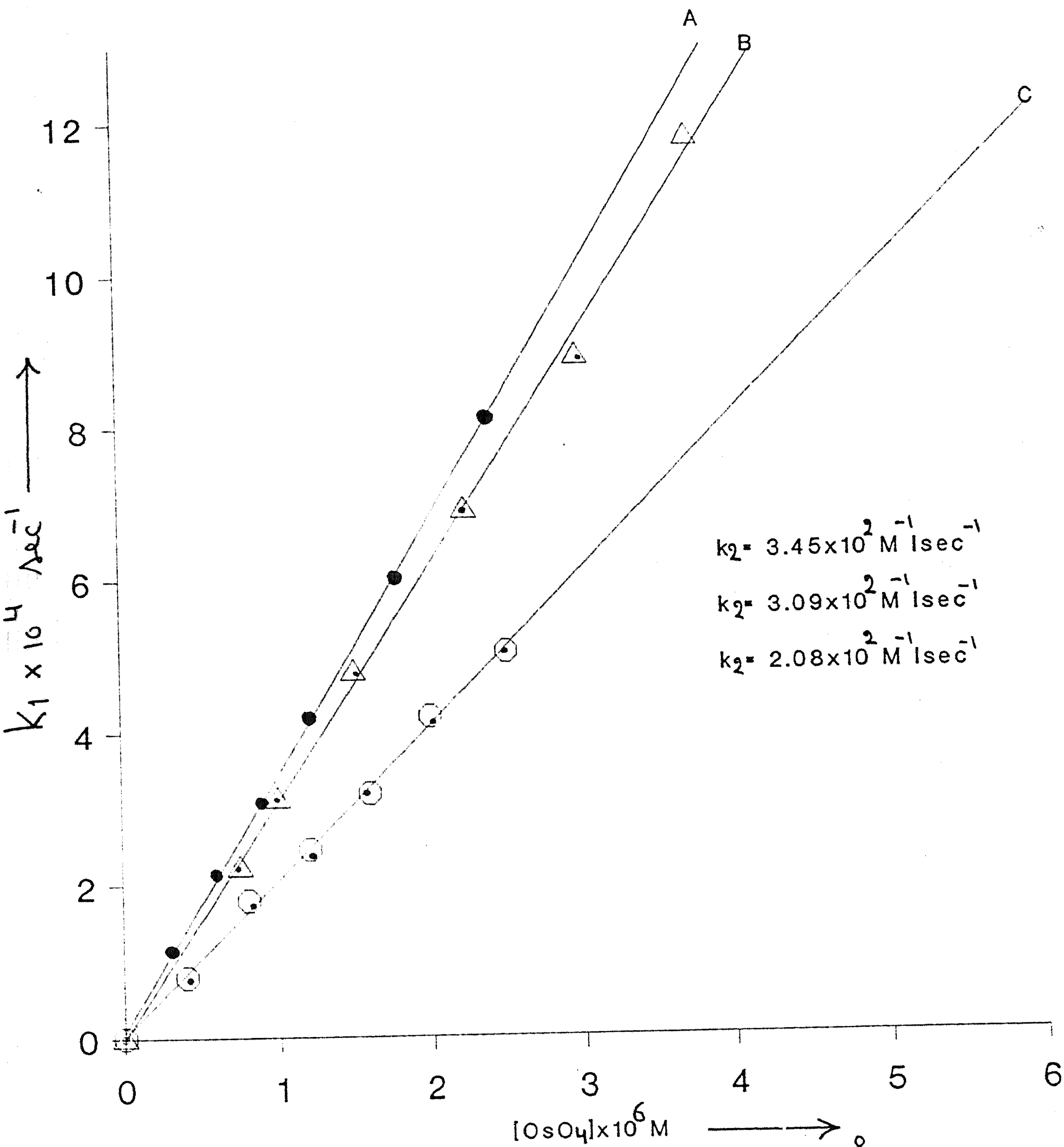


FIG.6.1 : PLOT OF k_1 Vs. $[OsO_4]$ AT 35°C
(A) : Under the conditions of table 6.16 (cyp)
(B) : Under the conditions of Table 6.17 (cyh)
(C) : Under the conditions of Table 6.18 (2-MCYh)

CHAPTER VII

DEPENDENCE OF REACTIONS ON IONIC STRENGTH OF THE MEDIUM IN OXIDATION OF CYCLOALCOHOLS BY ALKALINE CHLORAMINE-T SOLUTION IN PRESENCE OF OSMIUM TETROXIDE

7: DEPENDENCE OF REACTIONS ON IONIC STRENGTH OF THE MEDIUM IN OXIDATION OF CYCLOALCOHOLS BY ALKALINE CHLORAMINE-T SOLUTION IN PRESENCE OF OSMIUM TETROXIDE

In order to investigate the effect of ionic strength of the medium on the rate constant of oxidation of cycloalcohols by alkaline solution of chloramine-T in presence of OsO_4, a number of experiments have been carried out in the presence of different concentrations of sodium perchlorate which changes ionic strength of the medium. The results of such experiments have been summarised in tables 7.1, 7.2 and 7.3 in oxidation of cyclopentanol, cyclohexanol and 2-methyl cyclohexanol respectively. It is observed that all the title reactions are not influenced even slightly, indicating zero effect of variation of ionic strength of the medium.

TABLE 7.1

$[CAT] = 2.00 \times 10^{-3}$ M, $[CYP] = 1.00 \times 10^{-2}$ M

$[NaOH] = 0.50 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 35 °C

$[NaClO_4] \times 10^{2}$ M	Ionic strength (u) $\times 10^{2}$ M	$k_1 \times 10^{4}$ sec^{-1}
0.00	0.50	2.01
0.25	0.75	2.10
0.50	1.00	2.06
0.75	1.25	2.02
1.00	1.50	2.02
1.50	2.00	2.06
2.00	2.50	2.02
3.00	3.50	2.00
4.00	4.50	2.00
5.00	5.50	2.04

<u>TABLE 7.2</u>

[CAT] = 2.00×10^{-3} M, [NaOH] = 1.25×10^{-2} M,

[illegible] = 2.00×10^{-2} M, [OsO_4] = 0.75×10^{-6} M

Temperature 35^{o}C

[$NaClO_4$] $\times 10^{-3}$ M	Ionic strength (u) $\times 10^{2}$ M	$k_1 \times 10^{4}$ sec^{-1}
0.00	1.25	4.78
0.25	1.50	4.70
0.50	1.75	4.72
1.00	2.25	4.79
1.75	3.00	4.71
2.25	3.50	4.79
3.00	4.25	4.75
4.00	5.25	4.73
5.00	6.25	4.77
6.25	7.50	4.76

TABLE 7.3

[CAT] = 2.00×10^{-3} M, [NaOH] = 1.00×10^{-2} M,

[OsO_4] = 0.80×10^{-6} M, [2 Mcyh] = 2.00×10^{-2} M

Temperature 35°C

[$NaClO_4$] $\times 10^{2}$ M	Ionic strength (μ) $\times 10^{2}$ M	$k_1 \times 10^{4}$ sec^{-1}
0.00	1.00	3.12
0.25	1.25	3.08
0.50	1.50	3.11
0.75	1.75	3.09
1.00	2.00	3.13
1.50	2.50	3.15
2.00	3.00	3.12
2.50	3.50	3.11
3.00	4.00	3.10
4.00	5.00	3.06
5.00	6.00	3.09

CHAPTER VIII

DEPENDENCE OF OXIDATION OF CYCLOALCOHOLS BY CHLORAMINE-T CATALYSED BY ALKALINE OSMIUM TETROXIDE ON ADDED AMOUNT OF PARA-TOLUENESULPHONAMIDE

8 : DEPENDENCE OF OXIDATION OF CYCLOALCOHOLS BY CHLORAMINE-T CATALYSED BY ALKALINE OSMIUM TETROXIDE ON ADDED AMOUNT OF PARA-TOLUENESULPHONAMIDE

Para-toluenesulphonamide is reduction product of chloramine-T in the present investigation. Hence it was thought worthwhile to study the effect of addition of para-toluenesulphonamide (PTS) on the rate constants of oxidation of cycloalcohols under conditions already employed in previous chapters. For this purpose a set of experiments with various amounts of para-toluenesulphonamide under same experimental conditions have been carried out and the results are given in tables 8.1, 8.2 and 8.3 in summarised form. It is observed that in oxidation of all cycloalcohols used here, there is negligible effect of addition of para-toluenesulphonamide.

TABLE 8.1

$[CAT] = 2.00 \times 10^{-3}$ M, $[Cyp] = 2.00 \times 10^{-2}$ M

$[OsO_4] = 1.20 \times 10^{-6}$ M, $[NaOH] = 1.00 \times 10^{-2}$

Temperature 35 °C

$[PTS] \times 10^3$ M	$k_1 \times 10^4$ sec^{-1}
0.00	8.00
0.25	7.98
0.50	8.06
0.75	8.10
1.00	8.02
1.50	8.04
2.00	8.00
2.50	7.98
3.00	8.01

TABLE 8.2

$[CAT] = 2.00 \times 10^{-3}$ M, $[Cyh] = 1.00 \times 10^{-2}$ M

$[OsO_4] = 0.75 \times 10^{-6}$ M, $[NaOH] = 2.00 \times 10^{-2}$ M

Temperature 35 ^{o}C

$[PTS] \times 10^{3}$ M	$k_1 \times 10^{4}$ sec^{-1}
0.00	3.68
0.25	3.66
0.50	3.70
0.75	3.68
1.00	3.69
1.50	3.67
2.00	3.64
2.50	3.60
3.00	3.71

TABLE 8.3

$[CAT] = 2.00 \times 10^{-3}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M,

$[2\text{-Mcyh}] = 1.00 \times 10^{-2}$ M, $[NaOH] = 2.50 \times 10^{-2}$ M

Temperature 35 ^{o}C

$[PTS] \times 10^{3}$ M	$k1 \times 10^{4}$ sec^{-1}
0.00	4.23
0.25	4.20
0.50	4.21
0.75	4.18
1.00	4.28
1.50	4.22
2.00	4.23
2.50	4.30
3.00	4.19

CHAPTER IX

DEPENDENCE OF OXIDATION OF CYCLOALCOHOLS BY ALKALINE CHLORAMINE-T IN PRESENCE OF OSMIUM TETROXIDE AS CATALYST ON TEMPERATURE

9 : DEPENDENCE OF OXIDATION OF CYCLOALCOHOLS BY ALKALINE CHLORAMINE-T IN PRESENCE OF OSMIUM TETROXIDE AS CATALYST ON TEMPERATURE

The title reactions have been studied at 35 ^{0}C in previous chapters in details. Here in this chapter an attempt has been made to study these reactions at 30^{o}, 40^{o}, and 45^{o}C. The results of such experiments have been recorded in tables 9.1-9.3, 9.4-9.6 and 9.7-9.9 in oxidation of cyclopentanol cyclohexanol and 2-methylcyclohexanal and it has been observed that under similar physical condition of experiments on increasing the temperature of reactions the velocity constant increases markedly. Values of (-dc/dt) and k1 have been determined by the same method as described earlier.

Table 9.1

$[CAT] = 2.00 \times 10^{-3}$ M, $[Cyp] = 2.00 \times 10^{-2}$ M,

$[NaOH] = 0.50 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 30 ^{o}C

Time [min]	Volume of Hypo Solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	9.86		
5	9.20		
10	8.18		
15	7.46	4.82	2.67
20	6.60		
25	6.00		
35	5.20		
50	4.46		
60	4.02		
75	3.72		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M

Table 9.2

$[CAT] = 2.00 \times 10^{-3}$ M, $[Cyp] = 2.00 \times 10^{-2}$ M,

$[NaOH] = 0.50 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 40 ^{o}C

Time [min]	Volume of Hypo Solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	9.86		
5	9.18		
10	8.02		
15	7.38	10.42	5.79
20	6.48		
25	6.02		
30	4.46		
35	4.48		
50	3.82		
65	3.26		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M

Table 9.3

$[CAT] = 2.00 \times 10^{-3}$ M, $[Cyp] = 2.00 \times 10^{-2}$ M,

$[NaOH] = 0.50 \times 10^{-2}$ M, $[OsO_4] = 1.20 \times 10^{-6}$ M

Temperature 45°C

Time [min]	Volume of Hypo Solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$kl \times 10^{4}$ sec^{-1}
0	9.86		
5	9.00		
10	7.88		
15	7.20		
20	6.42	15.40	8.56
25	5.86		
30	5.20		
35	4.42		
40	3.72		
45	3.02		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M

Table 9.4

$[CAT] = 2.00 \times 10^{-3}$ M, $[Cyh] = 1.00 \times 10^{-2}$ M,

$[NaOH] = 1.25 \times 10^{-2}$ M, $[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature 30 ^{o}C

Time [min]	Volume of Hypo Solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.16		
5	[illegible]		
10	9.82		
20	9.10		
35	8.32		
50	[illegible]	3.94	1.69
75	4.86		
100	3.88		
140	2.68		
180	[illegible]		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M

Table 9.5

$[CAT] = 2.00 \times 10^{-3}$ M, $[Cyh] = 1.00 \times 10^{-2}$ M,

$[NaOH] = 1.25 \times 10^{-2}$, $[OsO_4] = 0.75 \times 10^{-6}$ M

Temperature 40 ^{o}C

Time [min]	Volume of Hypo Solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.16		
5	9.90		
10	9.62		
20	8.72		
30	7.86	6.80	3.78
45	6.00		
60	4.54		
90	3.00		
120	2.00		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M

Table 9.6

[CAT] = 2.00×10^{-3} M, [Cyh] = 1.00×10^{-2} M,
[NaOH] = 1.25×10^{-2} M, [OsO_4] = 0.75×10^{-6} M

Temperature 45^{o}C

Time [min]	Volume of Hypo Solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.16		
5	9.82		
10	9.58		
20	8.68		
30	7.76	8.82	4.98
45	5.58		
60	4.20		
80	3.14		
100	2.26		
120	1.42		

$[CAT]^{*} = 1.80 \times 10^{-3}$ M

Table 9.7

$[CAT] = 1.60 \times 10^{-2}$ M, [2 Meyh] $= 1.00 \times 10^{-2}$ M,

$[NaOH] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 30 ^{o}C

Time [min]	Volume of Hypo Solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
10	9.56		
20	9.00		
30	8.38	2.12	1.41
40	6.76		
50	5.68		
60	4.96		
85	4.00		
120	2.86		

$[CAT]^{*} = 1.50 \times 10^{-3}$ M

Table 9.8

$[CAT] = 1.60 \times 10^{-3}$ M, $[NaOH] = 1.00 \times 10^{-2}$ M,

$[2\text{-}MCyh] = 1.00 \times 10^{-2}$ M, $[OsO_4] = 0.80 \times 10^{-6}$ M

Temperature 40^{o} C

Time [min]	Volume of Hypo Solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
5	9.50		
10	9.06		
15	8.42		
20	6.84	4.20	2.80
25	5.76		
30	5.02		
45	3.86		
60	2.96		

$[CAT]^{*} = 1.50 \times 10^{-3}$ M

Table 9.9

[CAT] = 1.60×10^{-3} M, [NaOH] = 1.00×10^{-2} M,

[2 MCyh] = 1.00×10^{-2} M, [OsO4] = 0.80×10^{-6} M

Temperature 45^{o} C

Time [min]	Volume of Hypo Solution in ml	$(-dc/dt) \times 10^{7}$ Ml^{-1} sec^{-1}	$k1 \times 10^{4}$ sec^{-1}
0	10.00		
5	9.40		
10	8.84		
15	8.36	7.00	4.67
20	6.46		
25	5.30		
30	4.38		
45	3.00		
60	2.52		

$[CAT]^{*}$ = 1.50×10^{-3} M

The results of tables 9.1-9.3 & 3.5, tables 9.4-9.6 & 3.10 and tables 9.7-9.9 & 3.15 have been summarised in tables 9.10, 9.11 and 9.12 respectively.

Table 9.10

$[CAT] = 2.00 \times 10^{-3}$ M, $[Cyp] = 2.00 \times 10^{-2}$ M

$[OsO_4] = 1.20 \times 10^{-6}$ M, $[NaOH] = 0.5 \times 10^{-2}$ M

Temperature ^{o}C	$k_1 \times 10^{4}$ sec^{-1}
30	2.67
35	4.17
40	5.79
45	8.56

Table 9.11

$[CAT] = 2.00 \times 10^{-3}$ M, $[Cyh] = 1.00 \times 10^{-2}$ M
$[OsO_4] = 0.75 \times 10^{-6}$ M, $[NaOH] = 1.25 \times 10^{-2}$ M

Temperature ^{o}C	$k_1 \times 10^{4}$ sec^{-1}
30	1.69
35	2.22
40	3.78
45	4.90

<u>Table 9.12</u>

[CAT] = $1{\cdot}60 \times 10^{-3}$ M, [OsO_4] = $0{\cdot}80 \times 10^{-6}$ M

[2-Mcyh] = $1{\cdot}00 \times 10^{-2}$ M, [NaOH] = $1{\cdot}00 \times 10^{-2}$ M

Temperature ^{o}C	$k_1 \times 10^{4}$ sec^{-1}
30	1.41
35	1.78
40	2.80
45	4.67

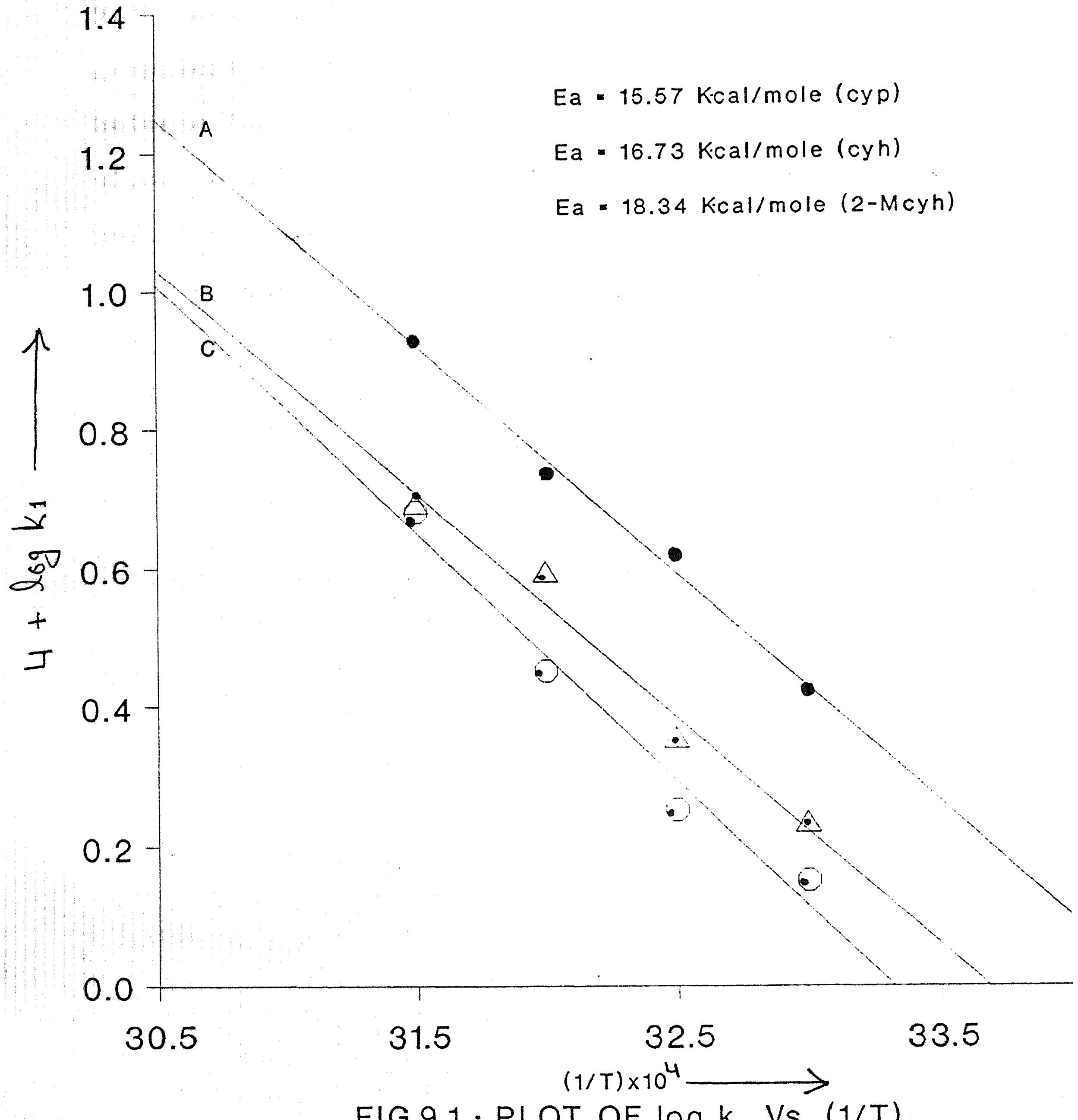


FIG.9.1 : PLOT OF log k Vs. (1/T)
(A) : Under the conditions of Table 9.10 (cyp)
(B) : Under the conditions of Table 9.11 (cyh)
(C) : Under the conditions of Table 9.12 (2-MCYh)

The kinetic results obtained in summarised tables 9.10, 9.11 and 9.12 at 30^{o}, 35^{o}, 40^{o} and $45^{o}C$ have been graphically represented (Fig.9.1) by plotting a graph between log k1 and (1/T). A straight line in each case with slope equal to (-Ea/2.303R) is obtained. Thus it is possible to calculate energy of activation (Ea) from the slope of straight line. The values of energy of activation i.e. -Ea in oxidation of cyclopentanol, cyclohexanol and 2-methylcyclohexanol by alkaline solution of chloramine-T in presence of osmium tetroxide are 15.57, 16.73 and 18.34 Kcal/mole respectively.

CHAPTER X

DISCUSSION AND RATE LAW DERIVATION

DISCUSSION AND RATE LAW DERIVATION

Study of a particular reaction through 'kinetic investigations' provides sufficient informations about the path ways through which a reaction is expected to occur. The kinetic orders determined with respect to various reactants reveal the rate determining step and help in elucidating the overall mechanism of the reactions.

The most important feature in deriving the rate law is the application of steady state treatment. Under this treatment, it is assumed that the formation and consumption of particular species are equal. Thus the study of the step by step oxidation in the above mentioned way gives results which could be interpreted to give a clear picture of the mechanism. Most of these factors have been taken into consideration to arrive at some interesting conclusions on the mechanism of redox systems under investigation here in the present thesis.

10.1: SUMMARY OF RESULTS OBTAINED IN OSMIUM TETROXIDE CATALYSED OXIDATION OF CYCLOALCOHOLS BY ALKALINE SOLUTION OF CHLORAMINE-T

The kinetic observations made in the present thesis are described below.

(i) First order kinetics with respect to Chloramine-T in Oxidation of cycloalcohols was observed.

(ii) First order dependence on each of cycloalcohols was exhibited.

(iii) All oxidation processes followed first order kinetic with respect to sodium hydroxide concentrations.

(iv) It has been observed that on increasing the concentration of osmium tetroxide the reaction velocity constant increases linearly, showing first-order dependence on osmium tetroxide.

(v) Zero effect of variation of ionic strength of the medium on velocity constant was noticed.

(vi) Addition of para-toluenesulphonamide in the reaction mixture did not influence the reaction rate constant of oxidation of cycloalcohols.

(vii) Marked effect of rise of temperature on rate constant was observed.

10.2: MECHANISM OF OSMIUM TETROXIDE CATALYSED OXIDATION OF CYCLOPENTANOL, CYCLOHEXANOL AND 2-METHYLCYCLOHEXANOL BY ALKALINE SOLUTION OF CHLORAMINE-T

A close examination of results described in section 10.1 clearly shows that all processes of the title follow similar kinetic behaviour. Hence, it is expected that all the reactions must follow the same mechanistic paths, which have been discussed below.

Osmium tetroxide has been reported to exist in the alkaline media as octahedral complexes of the form, trans-$[OsO_4(OH)H_2O]^{1-}$ and $[OsO_4(OH)_2]^{2-}$ the existence of the following equilibrium in alkaline medium has been reported to be possible on the basis of experimental observation.

$$[OsO_4(OH)(H_2O)]^{1-} + OH^- \rightleftharpoons [OsO_4(OH)_2]^{2-} + H_2O \quad \text{-------} \quad (1)$$

In the alkaline media, it has also been reported that Os(VIII) dose not exist as OsO_4 even in traceable amount. Hence, it can be safely assumed that $[OsO_4(OH)_2]^{2-}$ is the only reactive species which acts as a catalyst in the present investigations

Chloramine-T has been described to exist in alkaline medium[3,4] as given below .

$$\underset{(CAT)}{RNNaCl} + H_2O \rightleftharpoons \underset{(CAT')}{RNHCl} + NaOH \quad \text{-------} \quad (2)$$

$RNHCl + NaOH = RNH_2 + Na^+ + OCl^-$ ---------- (3)

Where R stands for $CH_3C_6H_4SO_2$-group.

Thus in alkaline media there are three possible reactive species namely Chloramine-T (i.e. CAT) itself, RNHCl (i.e. CAT') and OCl^- of Chloramine-T when CAT' and OCl^- are assumed as reactive species, the observed kinetics are not explained . For example on assuming CAT as real oxidising species decreasing effect of OH^- is required, contrary to observed increasing effect of OH^- ions. Similarly the observed insignificant effect of para toluenesulphonamide (PTS)is also not in conformity with the requirement of ClO^- supported to be the real active species of chloramine-T.

Hence both these species CAT' and OCl^- are ruled out for taking and assuming them to be real oxidizing species of Chloramine-T. Thus only choice left is to be assume CAT as such to be real oxiding species of Chloramine-T which is also known as sodium salt of N-chloro-p-toluenesulphonamide. All kinetic results are also explained satisfactorily on assuming CAT as real active oxidising species of chloramine-T.

The following reaction routes are suggested on the basis of real species of osmium tetroxide and Chloramine-Tin alkaline media as stated above for the oxidation of cycloalcohols. Here 'S' represents alcohol.

$$[OsO_4(OH)(H_2O)]^{1-} + OH^- \overset{K_1}{\rightleftharpoons} [OsO_4(OH)_2]^{2-} + H_2O \quad \text{--(1)}$$

(C1) (C2)

$$C_2 + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X \text{ (Intermediate)} \quad \text{--(2)}$$

$$X + CAT \xrightarrow{k_3} RNH_2 + [OsO_4(OH)_2]^{2-} + \text{Products} \quad \text{--(3)}$$

slow and

rate determining step

The rate of the reaction in terms of rate of consumption of CAT may be given as

$$\frac{-d[CAT]}{dt} = k_3[CAT][X] \quad \text{--(4)}$$

On applying steady state treatment to [X], we have –

$$\frac{d[X]}{dt} = 0 = k_2[C_2][S] - k_{-2}[X] - k_3[X][CAT]$$

or $k_{-2}[X] + k_3[X][CAT] = k_2[C_2][S]$

or $[X]\{k_{-2} + k_3[CAT]\} = k_2[C_2][S]$

$$\text{or } [X] = \frac{k_2[C_2][S]}{k_{-2} + k_3[CAT]} \qquad \text{--(5)}$$

The total concentration of osmium tetroxide may be written as eqn.(6).

$$[OsO4]_T = [C_1] + [C_2] + [X] \qquad \text{--(6)}$$

Considering step (i), we have eqn.(7)

$$[C_1] = \frac{[C_2][H_2O]}{k_1[OH^-]} \qquad \text{--(7)}$$

On substituting the value of [X] from eqn.(5) and value of $[C_1]$ from eqn.(7) in eqn.(6), we have

$$[OsO4]_T = \frac{[C_2][H_2O]}{k_1[OH^-]} + [C_2] + \frac{k_2[C_2][S]}{k_{-2} + k_3[CAT]}$$

$$\text{or } [OsO4]_T = [C_2]\left\{\frac{[H_2O]}{k_1[OH^-]} + 1 + \frac{k_2[S]}{k_{-2} + k_2[CAT]}\right\}$$

$$\text{or } [C_2] = \frac{k_1[OsO4][OH^-](Z)}{[H_2O](Z) + k_1[OH^-](Z) + k_2k_1[S][OH^-]} \quad \text{--(8)}$$

Where $(Z) = (k_{-2} + k_2[CAT])$

On substituting the value of $[C_2]$ from eqn.(8) into eqn.(5), we have

$$[X] = \frac{k_2K_1[OsO4]_T[S][OH^-](Z)}{(Z)\{(Z)[H_2O] + (Z)K_1[OH^-] + k_2K_1[S][OH^-]\}}$$

$$\text{or } [X] = \frac{k_2K_1[OsO4]_T[S][OH^-]}{(Z)[H_2O] + K_1[OH^-](Z) + k_2K_1[S][OH^-]} \quad \text{--(9)}$$

On comparing eqns.(9) and (4), we have

$$\frac{-d[CAT]}{dt} = \frac{k_2k_3K_1[CAT][OsO4]_T[S][OH^-]}{(Z)([H_2O] + K_1[OH^-]) + k_2K_1[S][OH^-]} \quad \text{--(10)}$$

On assuming $[H2O] >> K_1[OH^-]$, eqn.(10) may be written as eqn.(11) on neglecting $K_1[OH^-]$

$$\frac{-d[CAT]}{dt} = \frac{k_2k_3K_1[CAT][OsO4]_T[S][OH^-]}{(Z)[H_2O] + k_2K_1[S][OH^-]} \quad \text{--(11)}$$

Further, inequality $(Z)[H_2O] >> k_2K_1[S][OH^-]$ appears to be valid and hence eqn.(11) accordingly can be written as eqn.(12).

$$\frac{-d[CAT]}{dt} = \frac{k_2k_3K_1[CAT][OsO4]_T[S][OH^-]}{(Z)[H_2O]} \quad --(12)$$

$$\text{or} \quad \frac{-d[CAT]}{dt} = \frac{k_1[CAT][OsO4]_T[S][OH^-]}{k_{-2} + k_3[CAT]} \quad --(13)$$

Where $k_1 = k_2k_3K_1/[H_2O]$

Since step (III) is slow, hence the value of k_3 is small. In the light of k_3 being small, inequality $k_{-2} >> k_3[CAT]$ can safely and rightly be assumed. Hence in the light of above statement eqn.(13) may be written as eqn.(14).

$$\frac{-d[CAT]}{dt} = \frac{k_1}{k_{-2}}[CAT][OsO4][S][OH^-]$$

$$\text{or} \quad \frac{-d[CAT]}{dt} = k\,[CAT][OsO4][S][OH^-] \quad --(14)$$

Where $k = k'/k_{-2}$

A close examination of rate law (14) clearly explains the first order kinetics in chloramine-T, osmium tetroxide, reducing cycloalcohols and hydroxide ions. It also explains negligible effect of para-toluenesulphonamide.

Negligible effect ionic strength variation is also clear from the step (3) (which is rate determining step) which involves a neutral species 'CAT' supporting no effect of ionic strength.

Thus all kinetic observations are well in agreement with rate law (14) which has been derived on the basis of suggested steps (1-3). Hence reaction scheme for osmium tetroxide catalysed oxidation of cycloalcohols by alkaline chloramine-T appears to be valid and convincing.

REFERENCES

1. W.P. Griffith : Qut. Rev. 19, 254 (1965).

2. F.A. Cotton and G. Wilbinson;
Advanced Inorganic Chem., 2nd Edn., Wiley Eastern Pvt. Ltd.,
N.Delhi, p.1007(1966).

3. R. Dietzel and K. Taufel; Apoth Ztg. 44, 989 (1929).

4. J.C. Morris, J.A. Solazar and M.A. Wineman, J. Am. Chem. Soc., 70, 2038 (1948).